Attorney Docket No. 05725.0435-00000

UNITED STATES PATENT APPLICATION

OF

GÉRARD LANG AND JEAN COTTERET

FOR

COMPOSITION FOR DYEING KERATIN FIBRES WITH A CATIONIC DIRECT DYE AND A THICKENING POLYMER

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The invention relates to a composition for dyeing keratin fibres, in particular human keratin fibres such as the hair, comprising, in a medium which is suitable for dyeing, at least one cationic direct dye of given formula and at least one specific thickening polymer.

The invention also relates to the dyeing processes and dyeing devices using the said composition.

Two types of dyeing may be distinguished in the haircare sector.

The first is semi-permanent or temporary dyeing, or direct dyeing, which uses dyes capable of giving the hair a natural coloration, a more or less pronounced colour change which may withstand shampooing several times. These dyes are also known as direct dyes; they can be used with or without an oxidizing agent. In the presence of an oxidizing agent, the aim is to obtain lightening dyeing. Lightening dyeing is carried out by applying a mixture, prepared at the time of use, of a direct dye and an oxidizing agent to the hair, and makes it possible in particular to obtain, by lightening the melanin in the hair, an advantageous effect such as a unified colour in the case of grey hair, or to bring out the colour in the case of naturally pigmented hair.

The second is permanent dyeing or oxidation dyeing. This is carried out with so-called "oxidation" dyes comprising oxidation dye precursors and couplers. Oxidation dye precursors, commonly known as "oxidation bases", are compounds which are initially colourless or weakly coloured which develop their dyeing power on

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the hair in the presence of oxidizing agents added at the time of use, leading to the formation of coloured compounds and dyes. The formation of these coloured compounds and dyes results either from an oxidative condensation of the "oxidation bases" with themselves or from an oxidative condensation of the oxidation bases with coloration-modifying compounds commonly known as "couplers", which are generally present in the dye compositions used in oxidation dyeing.

It is known practice to add direct dyes to oxidation dyes in order to vary the shades obtained with the said oxidation dyes or to enrich the shades with glints.

Among the cationic direct dyes available in the sector of dyeing keratin fibres, in particular human keratin fibres, the compounds whose structure is developed in the text hereinbelow are already known; nevertheless, these dyes lead to colorations which have characteristics that are still unsatisfactory as regards the intensity, the homogeneity of the colour distributed along the fibre, in which case the coloration is said to be too selective, and as regards the staying power, in terms of the resistance to the various attacking factors to which the hair may be subjected (light, bad weather, shampooing).

After considerable research conducted in this matter, the Applicant has now discovered that it is possible to obtain novel compositions for dyeing keratin fibres which are capable of giving more intense and yet unselective colorations which show good resistance to the various attacking factors to which the hair may be

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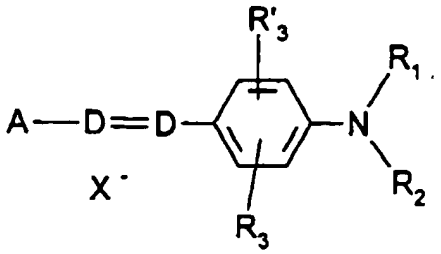
subjected, by combining at least one specific thickening polymer with at least one known cationic direct dye of the prior art, which have the respective formulae defined below.

This discovery forms the basis of the present invention.

A first subject of the present invention is thus a composition for dyeing keratin fibres, and in particular human keratin fibres such as the hair, containing, in a medium which is suitable for dyeing, **(i)** at least one cationic direct dye whose structure corresponds to formulae (I) to (IV) defined below, characterized in that it also contains **(ii)** at least one specific thickening polymer.

(i) The cationic direct dye which can be used according to the present invention is a compound chosen from those of formulae (I), (II), (III), (III') and (IV) below:

a) the compounds of formula (I) below:



(I)

in which:

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D represents a nitrogen atom or a -CH group,

R_1 and R_2, which may be identical or different, represent a hydrogen atom; a C_1-C_4 alkyl radical which can be substituted with a -CN, -OH or $-NH_2$ radical or form, with a carbon atom of the benzene ring, a heterocycle optionally containing oxygen or nitrogen, which can be substituted with one or more C_1-C_4 alkyl radicals; a 4'-aminophenyl radical,

R_3 and R'_3, which may be identical or different, represent a hydrogen atom, a halogen atom chosen from chlorine, bromine, iodine and fluorine, a cyano radical, or a C_1-C_4 alkyl, C_1-C_4 alkoxy or acetyloxy radical,

X^- represents an anion preferably chosen from chloride, methyl sulphate and acetate,

A represents a group chosen from the structures A1 to A19 below:

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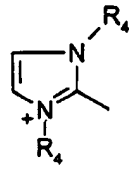
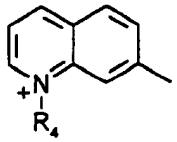
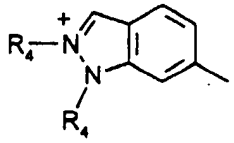
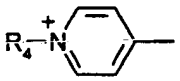
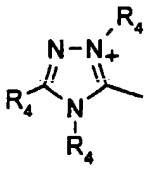
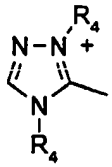

A_1 ;

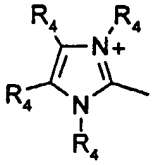

A_2 ;

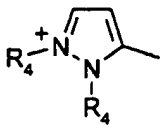

A_3 ;

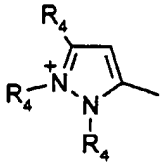

A_4 ;

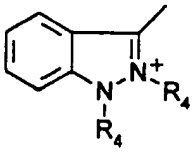

A_5 ;

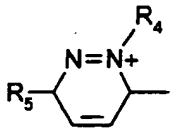

A_6 ;

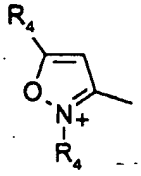

A_7 ;

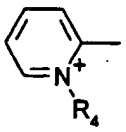

A_8 ;

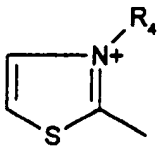

A_9 ;

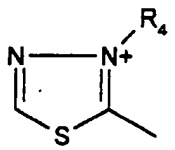

A_{10} ;

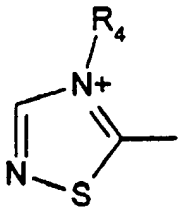

A_{11} ;


A_{12} ;

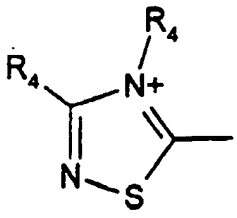

A_{13} ;


A_{14} ;

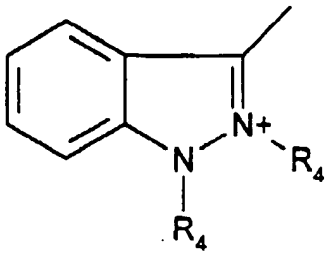

A_{15} ;



A_{16} ;

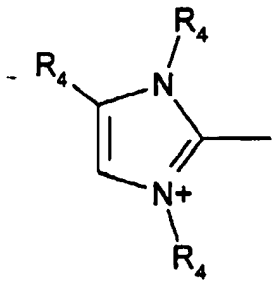


A_{17} ;



A_{18}

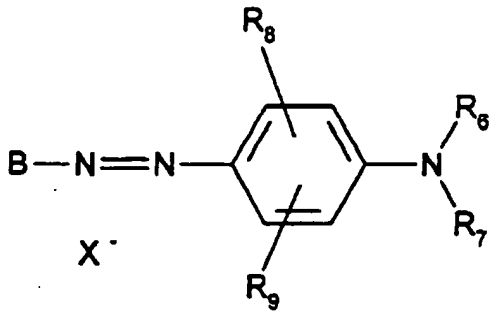
and



A_{19} ;

in which R_4 represents a C_1-C_4 alkyl radical which can be substituted with a hydroxyl radical and R_5 represents a C_1-C_4 alkoxy radical, with the proviso that when D represents -CH, when A represents A_4 or A_{13} and when R_3 is other than an alkoxy radical, then R_1 and R_2 do not simultaneously denote a hydrogen atom;

b) the compounds of formula (II) below:



(II)

in which:

R_6 represents a hydrogen atom or a C_1-C_4 alkyl radical,

R_7 represents a hydrogen atom, an alkyl radical which can be substituted with a -CN radical or with an amino group, a 4'-aminophenyl radical or forms with R_6 a heterocycle optionally containing oxygen and/or nitrogen, which can be substituted with a C_1-C_4 alkyl radical,

R_8 and R_9, which may be identical or different, represent a hydrogen atom, a halogen atom such as bromine, chlorine, iodine or fluorine, a C_1-C_4 alkyl or C_1-C_4 alkoxy radical or a -CN radical,

X^- represents an anion preferably chosen from chloride, methyl sulphate and acetate,

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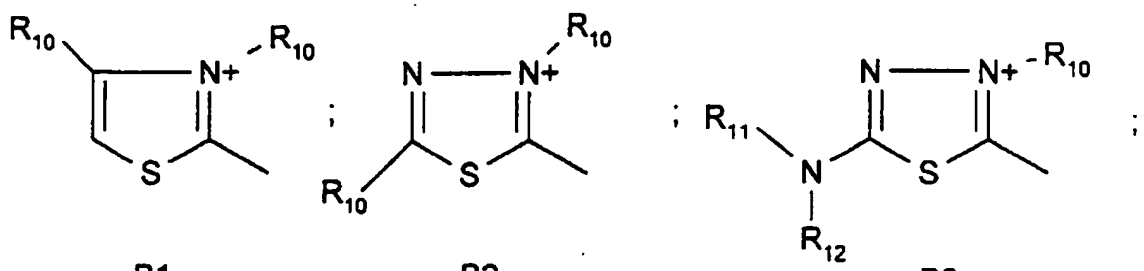
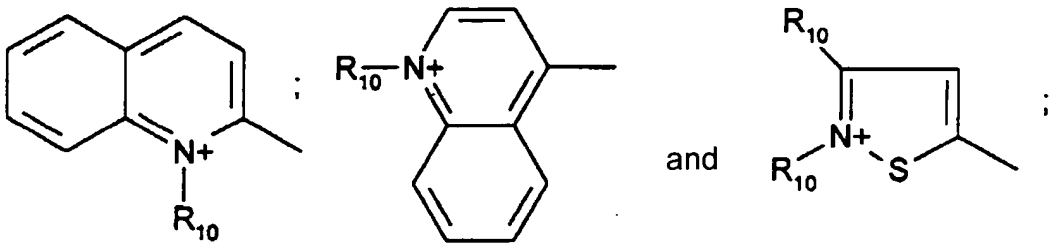
B represents a group chosen from the structures B1 to B6 below:



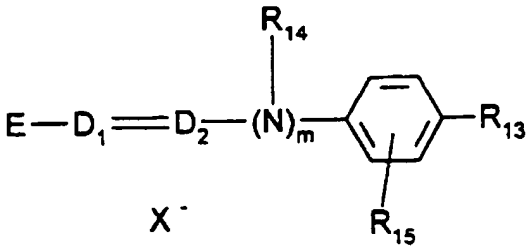
B1 B2 B3



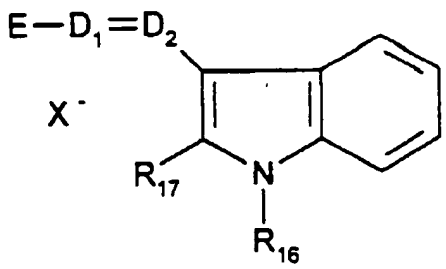
B4 B5 and B6

in which R_{10} represents a C_1-C_4 alkyl radical, R_{11} and R_{12}, which may be identical or different, represent a hydrogen atom or a C_1-C_4 alkyl radical;

c) **the compounds of formulae (III) and (III') below:**



(III)



(III')

in which:

R_{13} represents a hydrogen atom, a C_1-C_4 alkoxy radical, a halogen atom such as bromine, chlorine, iodine or fluorine, or an amino radical,

R_{14} represents a hydrogen atom, a C_1-C_4 alkyl radical or forms, with a carbon atom of the benzene ring, a heterocycle optionally containing oxygen and/or substituted with one or more C_1-C_4 alkyl groups,

R_{15} represents a hydrogen atom or a halogen atom such as bromine, chlorine, iodine or fluorine,

R_{16} and R_{17}, which may be identical or different, represent a hydrogen atom or a C_1-C_4 alkyl radical,

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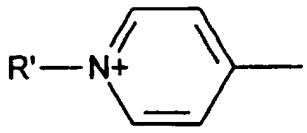
D_1 and D_2, which may be identical or different, represent a nitrogen atom or a -CH group,

m = 0 or 1,

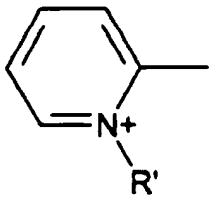
it being understood that when R_{13} represents an unsubstituted amino group, then D_1 and D_2 simultaneously represent a -CH group and m = 0,

X^- represents an anion preferably chosen from chloride, methyl sulphate and acetate,

E represents a group chosen from the structures E1 to E8 below:



E1 ;



E2 ;

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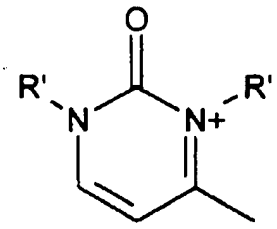
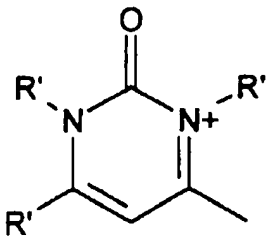
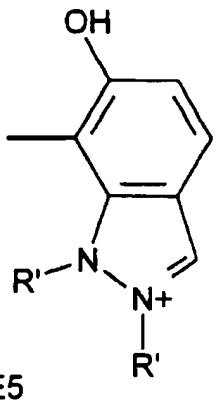


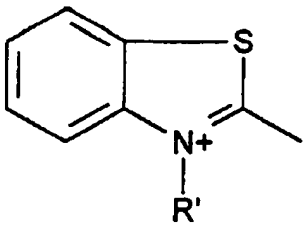
E3 ;



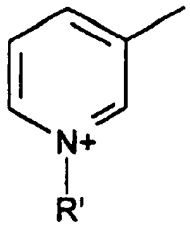
E4 ;



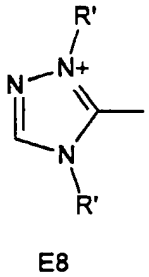
E5 ;



E6 ;



E7 and



E8 ;

in which R' represents a C_1-C_4 alkyl radical;

when m = 0 and when D_1 represents a nitrogen atom, then E can also denote a group of structure E9 below:

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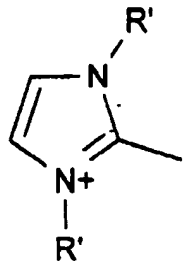
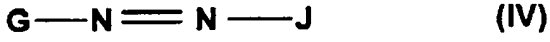
E9 

in which R' represents a C_1-C_4 alkyl radical;

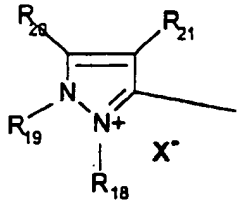
d) the compounds of formula (IV) below:



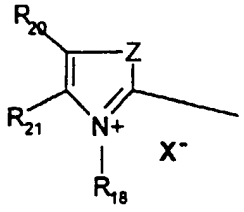
(IV)

in which:

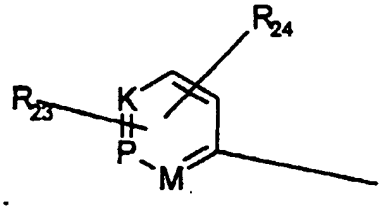
the symbol G represents a group chosen from the structures G_1 to G_3 below:



G_1



G_2



G_3

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in which structures G_1 to G_3,

R_{18} denotes a C_1-C_4 alkyl radical, a phenyl radical which can be substituted with a C_1-C_4 alkyl radical or a halogen atom chosen from chlorine, bromine, iodine and fluorine;

R_{19} denotes a C_1-C_4 alkyl radical or a phenyl radical;

R_{20} and R_{21}, which may be identical or different, represent a C_1-C_4 alkyl radical, a phenyl radical or together form, in G_1, a benzene ring substituted with one or more C_1-C_4 alkyl, C_1-C_4 alkoxy or NO_2 radicals or together form, in G_2, a benzene ring optionally substituted with one or more C_1-C_4 alkyl, C_1-C_4 alkoxy or NO_2 radicals;

R_{20} can also denote a hydrogen atom;

Z denotes an oxygen or sulphur atom or a group $-NR_{19}$;

M represents a -CH, -CR (R denoting C_1-C_4 alkyl) or $-N^+R_{22}(X^-)_r$ group;

K represents a -CH, -CR (R denoting C_1-C_4 alkyl) or $-N^+R_{22}(X^-)_r$ group;

P represents a -CH, -CR (R denoting C_1-C_4 alkyl) or $-N^+R_{22}(X^-)_r$ group; r denotes zero or 1;

R_{22} represents an O^- anion, a C_1-C_4 alkoxy radical or a C_1-C_4 alkyl radical;

R_{23} and R_{24}, which may be identical or different, represent a hydrogen atom, a halogen atom chosen from chlorine, bromine, iodine and fluorine, a C_1-C_4 alkyl or

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C_1-C_4 alkoxy radical or an -NO_2 radical;

X^- represents an anion preferably chosen from chloride, iodide, methyl sulphate, ethyl sulphate, acetate and perchlorate;

with the proviso that,

if R_{22} denotes O^-, then r denotes zero;

if K or P or M denote C_1-C_4 -N^+-alkyl X^-, then R_{23} or R_{24} is other than a hydrogen atom;

if K denotes -$N^+R_{22}(X^-)_r$, then M=P= -CH, -CR;

if M denotes -$N^+R_{22}(X^-)_r$, then K=P= -CH, -CR;

if P denotes -$N^+R_{22}(X^-)_r$, then K=M and denote -CH or -CR;

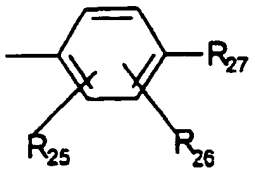
if Z denotes a sulphur atom with R_{21} denoting C_1-C_4 alkyl, then R_{20} is other than a hydrogen atom;

if Z denotes -NR_{22} with R_{19} denoting C_1-C_4 alkyl, then at least one of the radicals R_{18}, R_{20} or R_{21} of the group of structure G_2 is other than a C_1-C_4 alkyl radical;

the symbol J represents:

- (a) a group of

structure J_1 below:



J_1

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in which structure J_1,

R_{25} represents a hydrogen atom, a halogen atom chosen from chlorine, bromine, iodine and fluorine, a C_1-C_4 alkyl or C_1-C_4 alkoxy radical, a radical -OH, $-NO_2$, $-NHR_{28}$, $-NR_{29}R_{30}$, -NHCO (C_1-C_4) alkyl, or forms with R_{26} a 5- or 6-membered ring which may or may not contain one or more hetero atoms chosen from nitrogen, oxygen and sulphur;

R_{26} represents a hydrogen atom, a halogen atom chosen from chlorine, bromine, iodine and fluorine, a C_1-C_4 alkyl or C_1-C_4 alkoxy radical or forms, with R_{27} or R_{28}, a 5- or 6-membered ring which may or may not contain one or more hetero atoms chosen from nitrogen, oxygen and sulphur;

R_{27} represents a hydrogen atom, an -OH radical, a radical $-NHR_{28}$ or a radical $-NR_{29}R_{30}$;

R_{28} represents a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical or a phenyl radical;

R_{29} and R_{30}, which may be identical or different, represent a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical or a C_2-C_4 polyhydroxyalkyl radical;

- **(b)** a 5- or 6-membered nitrogenous heterocyclic group which can contain other hetero atoms and/or carbonyl groups and which can be substituted with one or more

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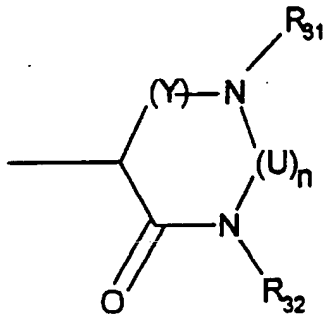
C_1-C_4 alkyl, amino or phenyl radicals,

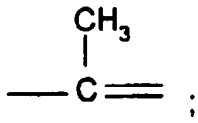
and in particular a group of structure J_2 below:



J_2

in which structure J_2,

R_{31} and R_{32}, which may be identical or different, represent a hydrogen atom, a C_1-C_4 alkyl radical or a phenyl radical;

Y denotes the -CO- radical or the radical 

;

n = 0 or 1, with, when n denotes 1, U denoting a -CO- radical.

In the structures (I) to (IV) defined above, the C_1-C_4 alkyl or alkoxy group preferably denotes methyl, ethyl, butyl, methoxy or ethoxy.

The cationic direct dyes of formulae (I), (II), (III) and (III') which can be used in the dye compositions in accordance with the invention are known compounds and are described, for example, in patent applications WO 95/01772, WO 95/15144 and EP-A-0,714,954. Those of formula (IV) which can be used in the dye compositions in

accordance with the invention are known compounds and are described, for example, in patent applications FR-2,189,006, FR-2,285,851 and FR-2,140,205 and its Certificates of Addition.

Among the cationic direct dyes of formula (I) which can be used in the dye compositions in accordance with the invention, mention may be made more particularly of the compounds corresponding to the structures (I1) to (I54) below:

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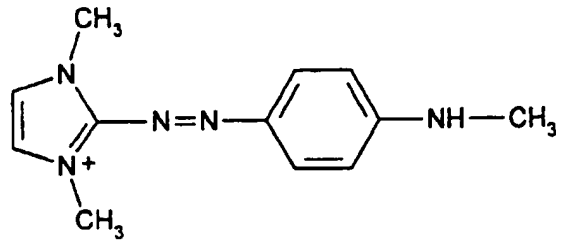
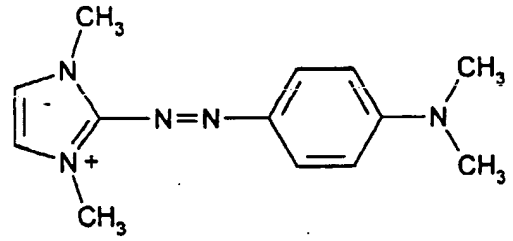
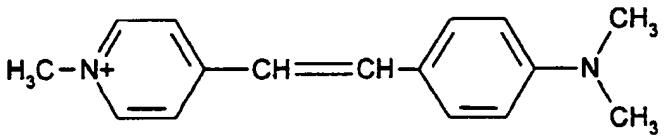


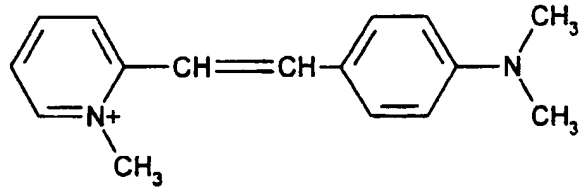
Cl⁻ (I1)



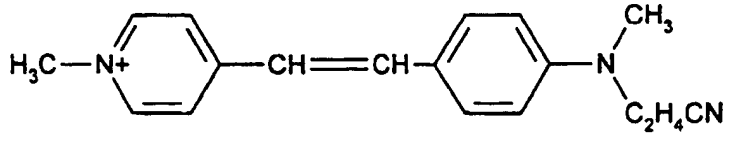
Cl⁻ (I2)



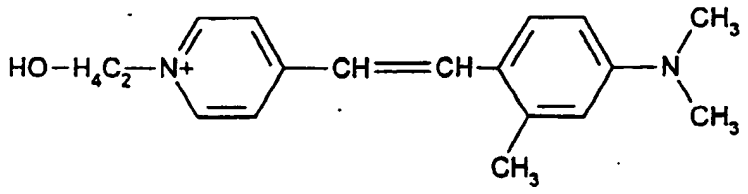
Cl⁻ (I3)



Cl⁻ (I4)



Cl⁻ (I5)



Cl⁻ (I6)

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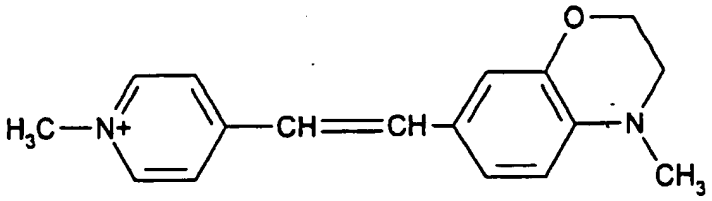
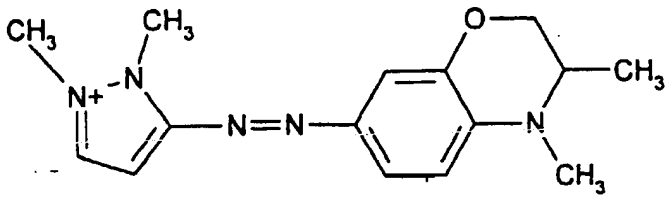
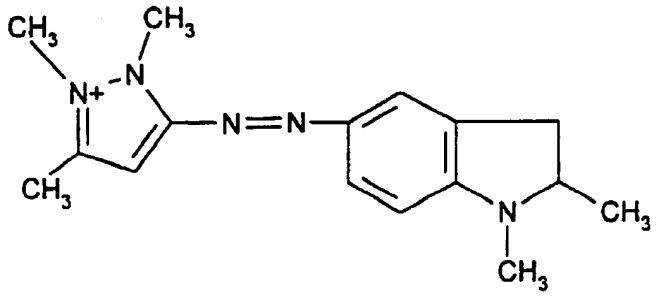


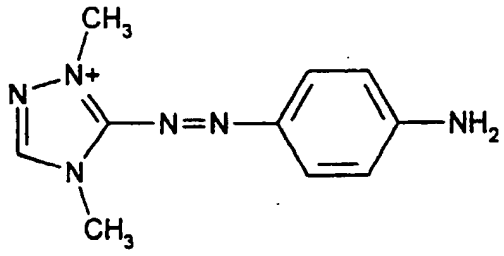
Cl^- (I7)



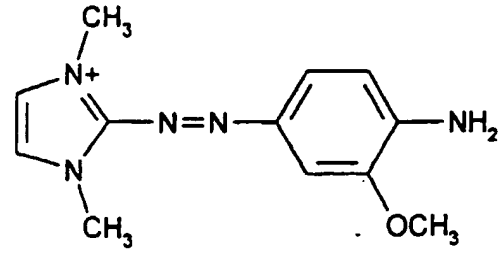
Cl^- (I8)



Cl^- (I9)



Cl^- (I10)



Cl^- (I11)

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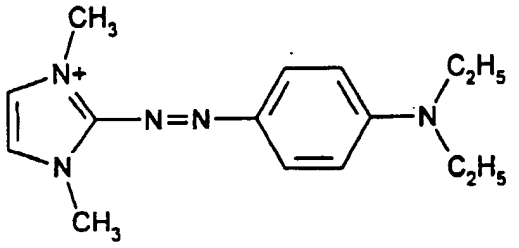
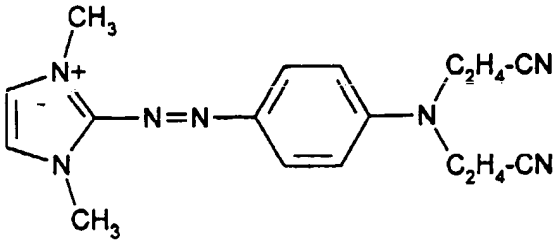
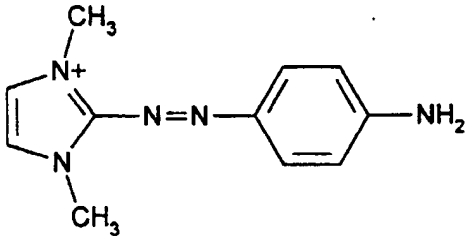


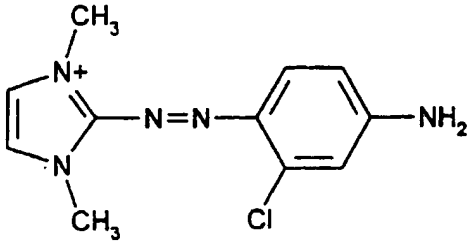
Cl^- (I12)



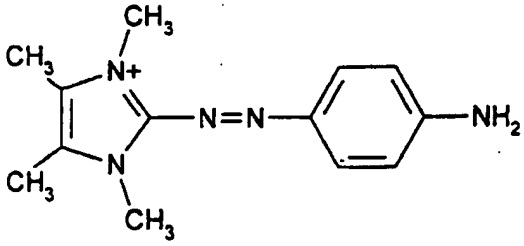
Cl^- (I13)



Cl^- (I14)



Cl^- (I15)



Cl^- (I16)

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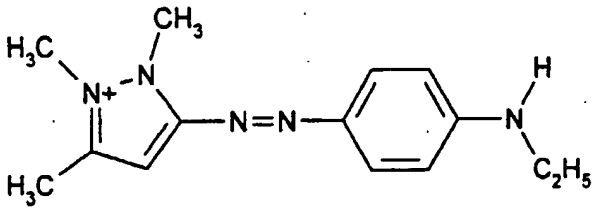
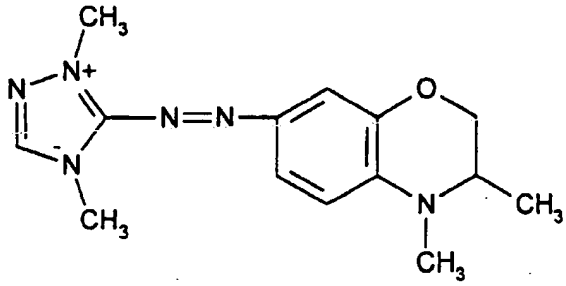
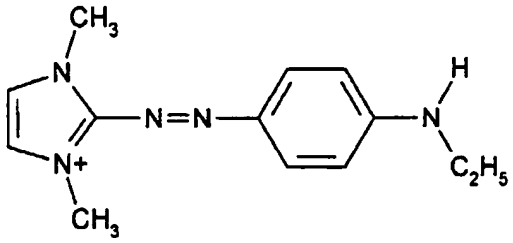


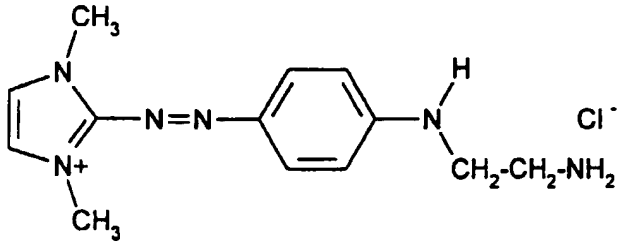
Cl^- (I17)



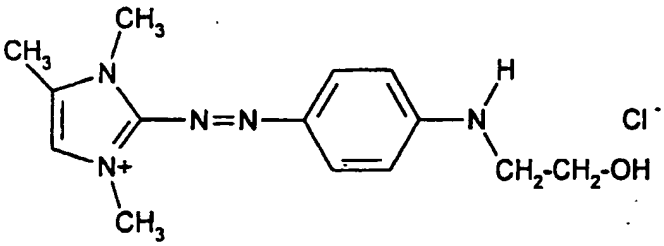
Cl^- (I18)



Cl^- (I19)



Cl^- (I20)



Cl^- (I21)

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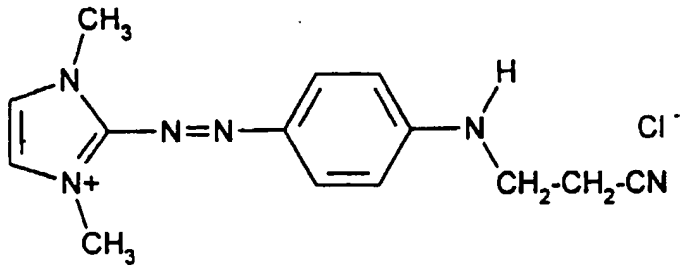
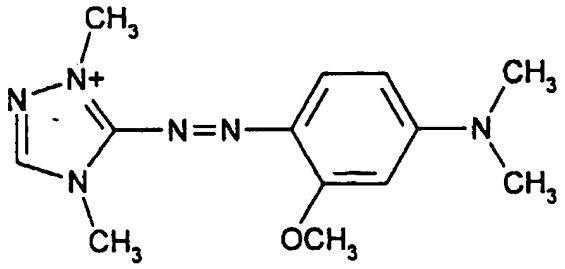
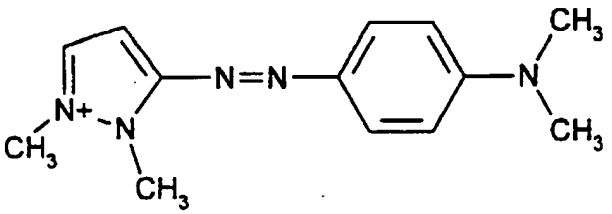


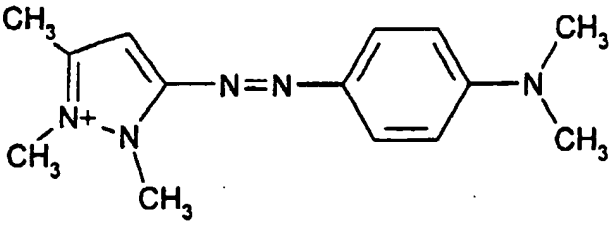
(I22)



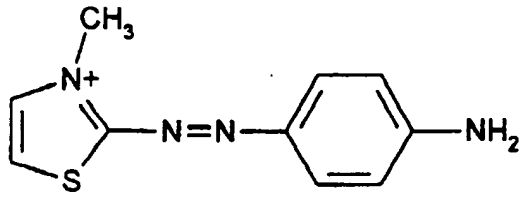
(I23)



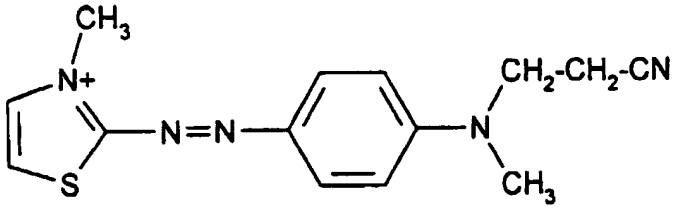
(I24)



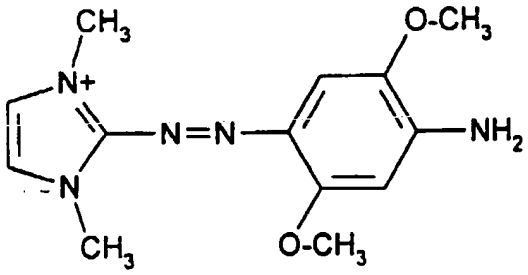
(I25)



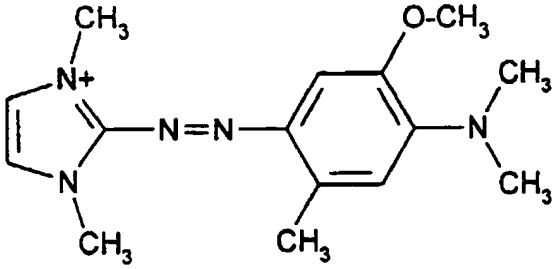
(I26)



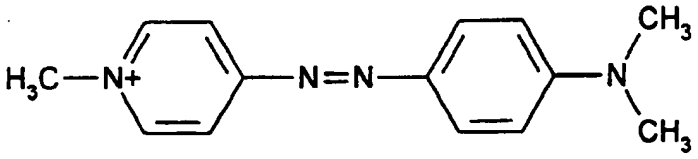
Cl⁻ (I27)



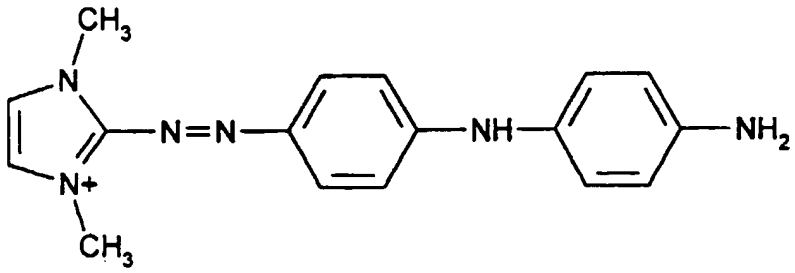
Cl⁻ (I28)



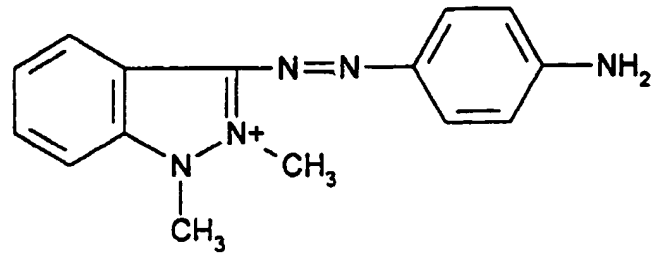
Cl⁻ (I29)



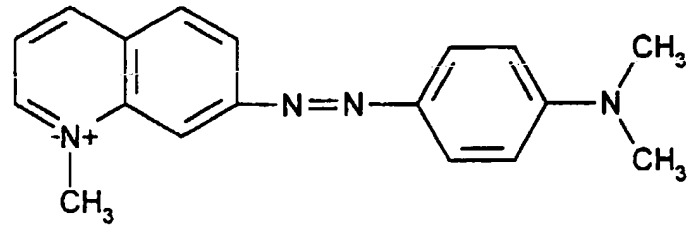
Cl⁻ (I30)



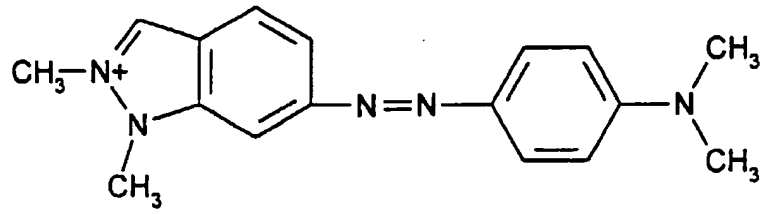
Cl⁻ (I31)



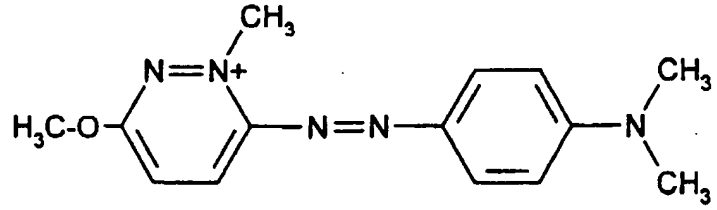
Cl⁻ (I32)



Cl⁻ (I33)



Cl⁻ (I34)



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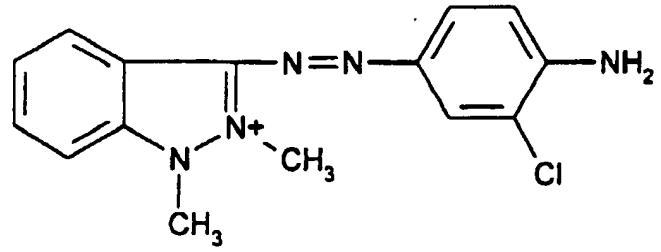

Cl⁻ (I36)

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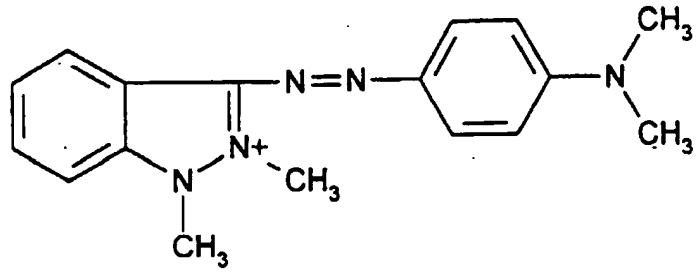
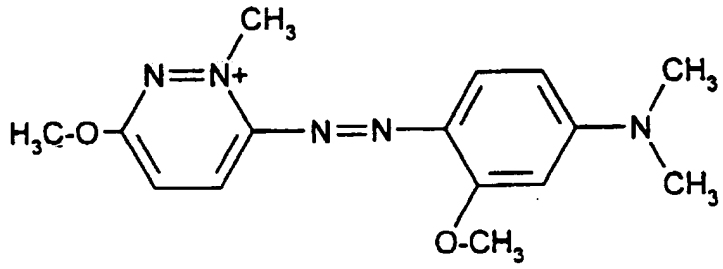
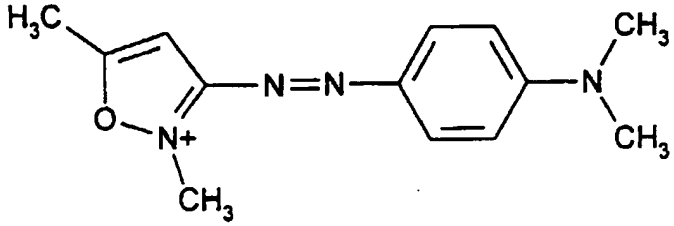


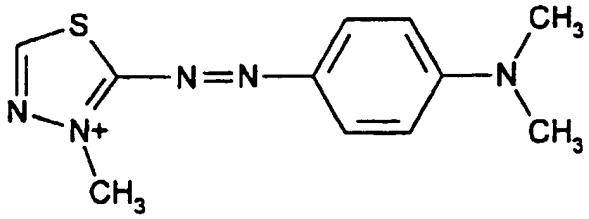
Cl⁻ (137)



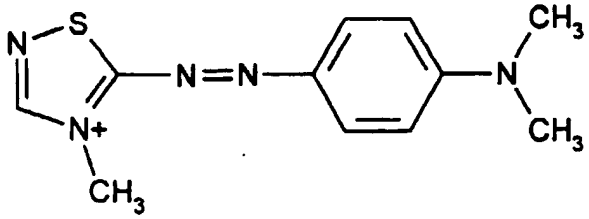
Cl⁻ (138)



Cl⁻ (139)



Cl⁻ (140)



Cl⁻ (141)

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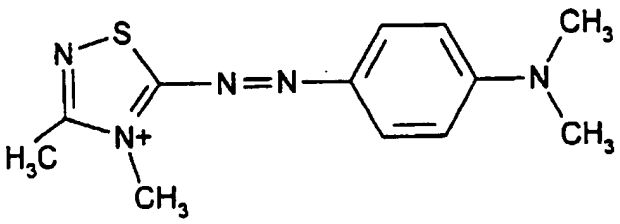
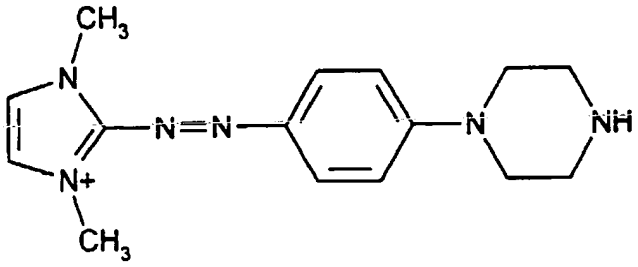
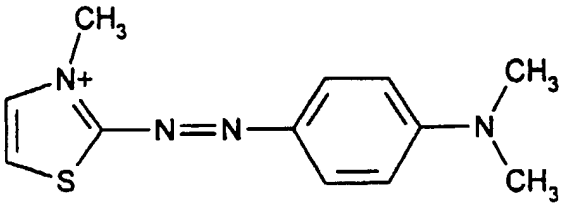


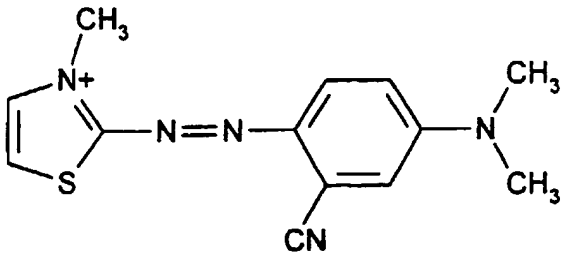
(I42)



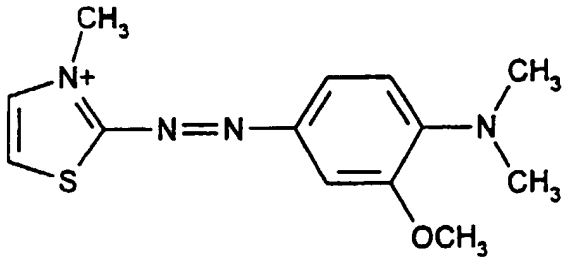
(I43)



(I44)



(I45)



(I46)

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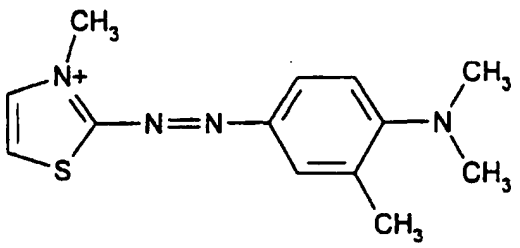
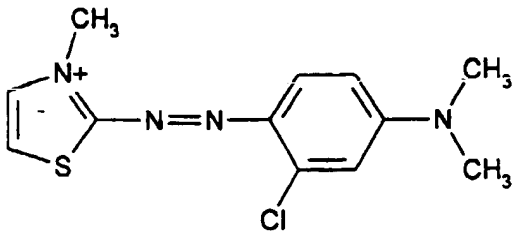
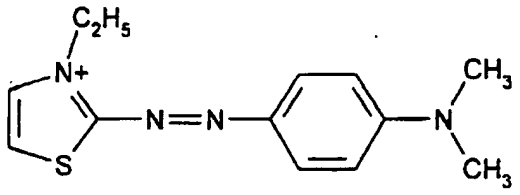


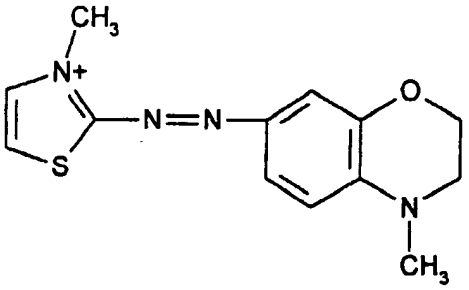
(147)



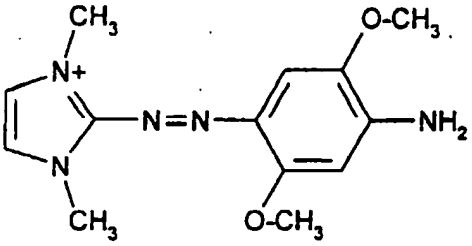
(148)



(149)



(150)



(151)

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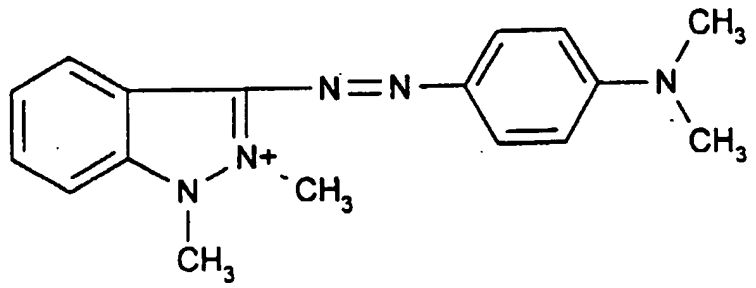
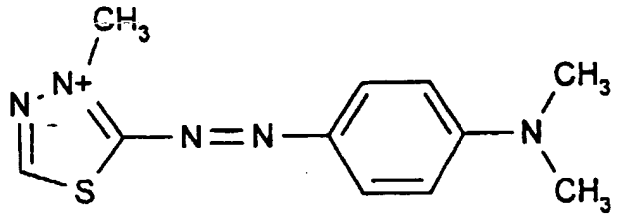
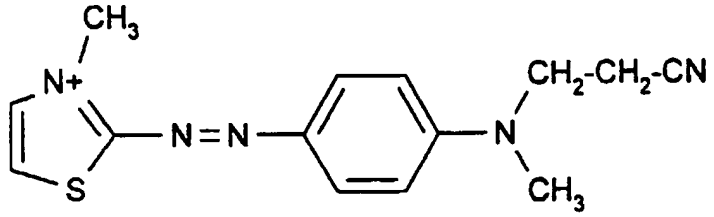


(I52)



(I53)



(I54)

Among the compounds of structures (I1) to (I54) described above, the ones most particularly preferred are the compounds corresponding to the structures (I1), (I2), (I14) and (I31).

Among the cationic direct dyes of formula (II) which can be used in the dye compositions in accordance with the invention, mention may be made more particularly of the compounds corresponding to the structures (II1) to (II9) below:

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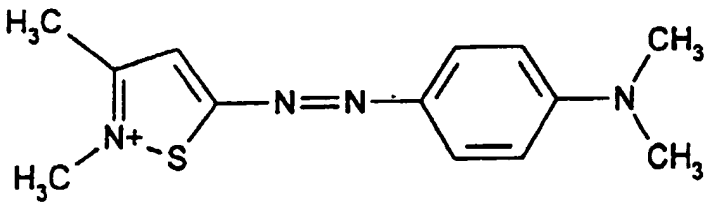

(II1)

;

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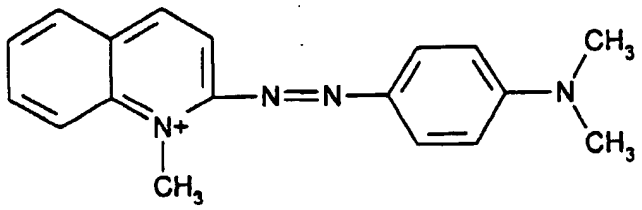
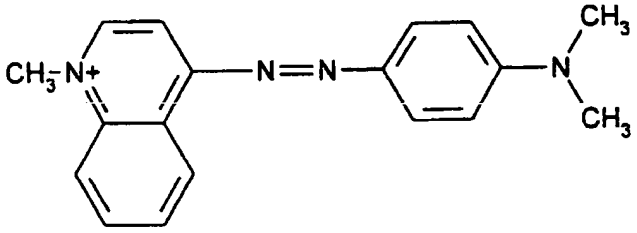
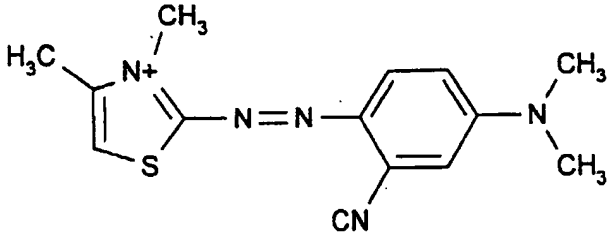


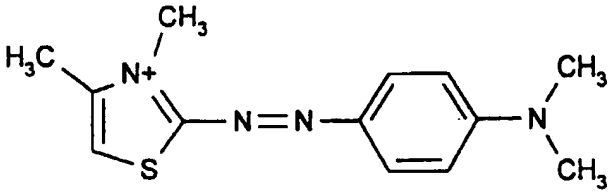
(II2)



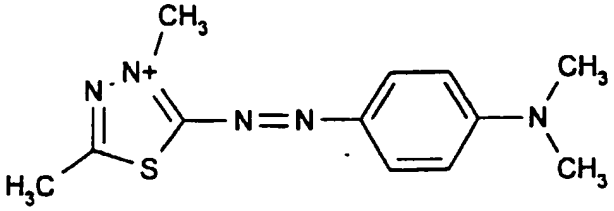
(II3)



(II4)



(II5)



(II6)

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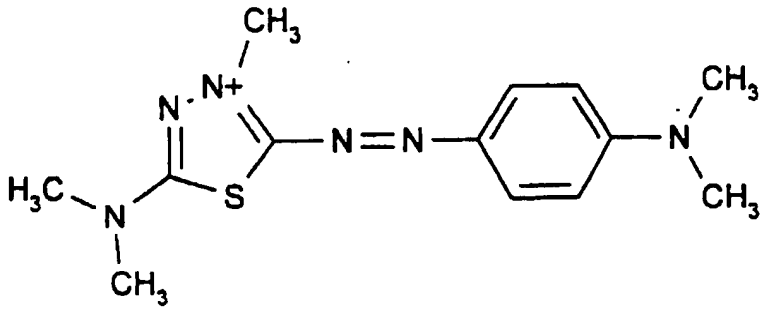
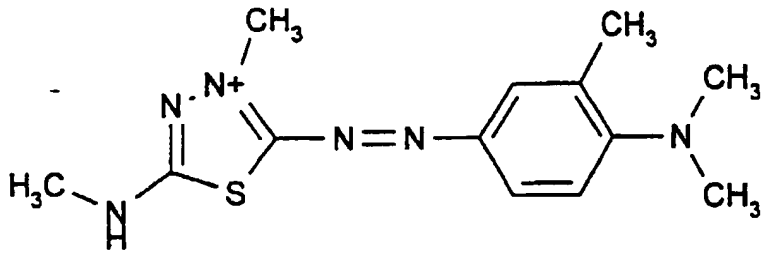


$CH_3SO_4^-$ (II7)

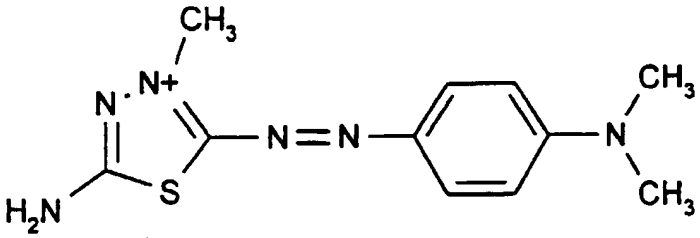
;



$CH_3SO_4^-$ (II8)

;

and



$CH_3SO_4^-$ (II9)

Among the cationic direct dyes of formula (III) which can be used in the dye compositions in accordance with the invention, mention may be made more particularly of the compounds corresponding to the structures (III1) to (III18) below:

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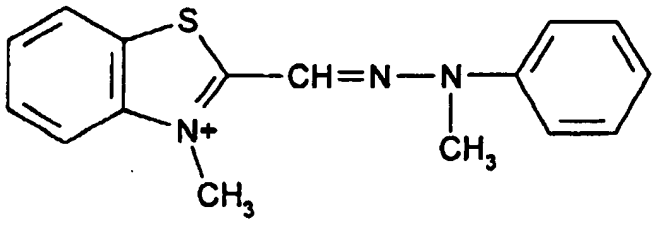
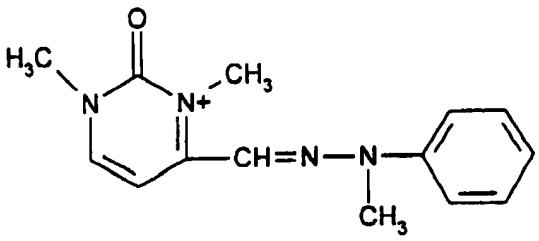


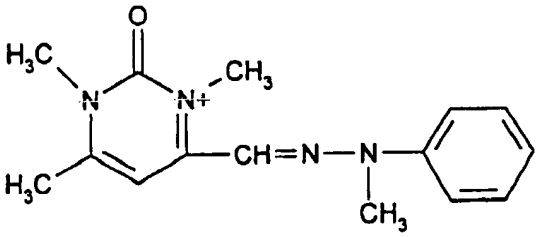
(III1)

;



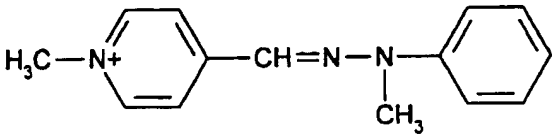
Cl⁻ (III2)

;



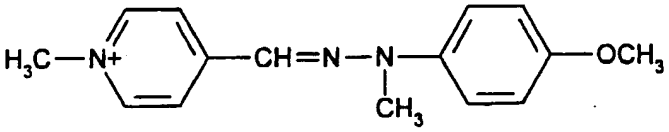
Cl⁻ (III3)

;



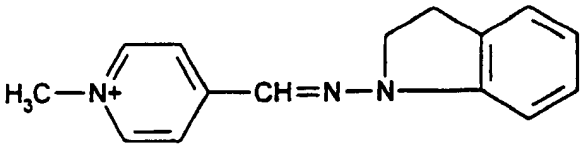
$CH_3SO_4^-$ (III4)

;



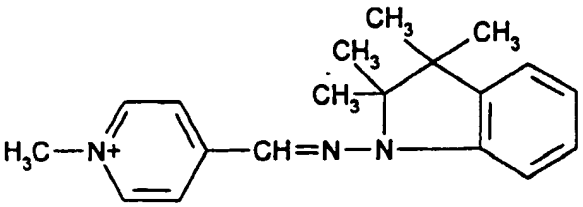
Cl⁻ (III5)

;



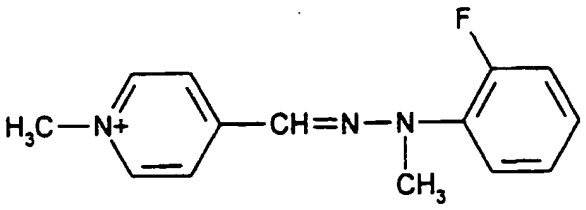
$CH_3SO_4^-$ (III6)

;



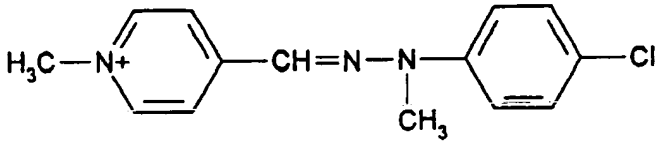
$CH_3SO_4^-$ (III7)

;



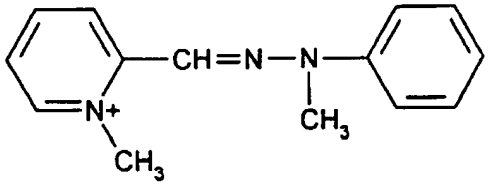
(III8)

;



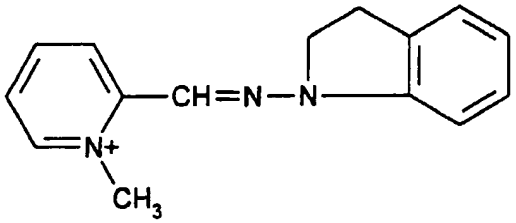
(III9)

;



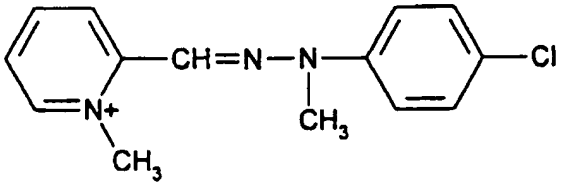
(III10)

;



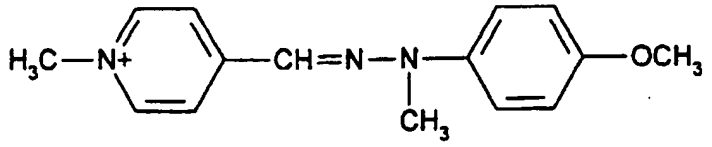
(III11)

;



(III12)

;



(III13)

;

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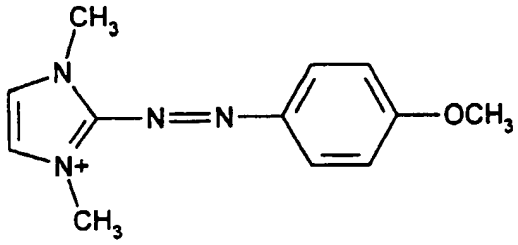
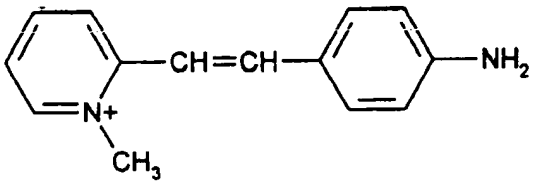


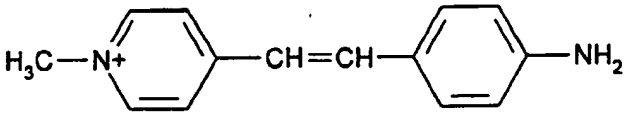
(III14)

;

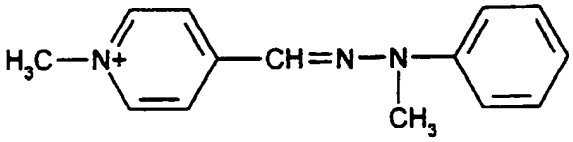


(III15)

;

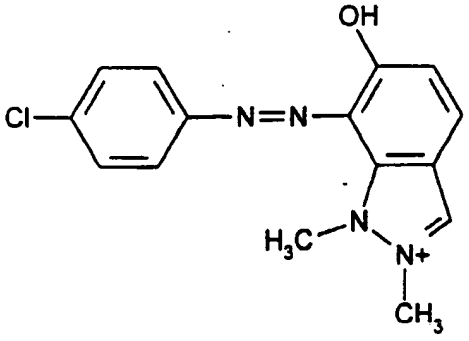


(III16)



(III17)

; and



(III18)

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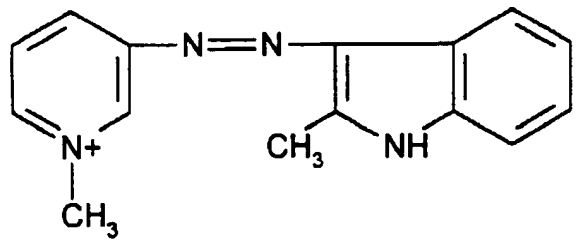
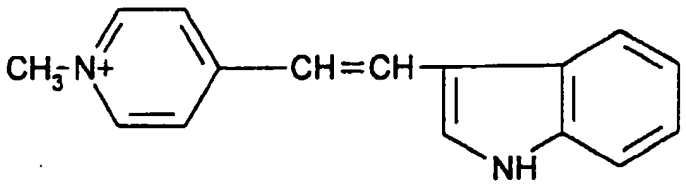
Among the specific compounds of structures (III1) to (III18) described above, the ones most particularly preferred are the compounds corresponding to the structures (III4), (III5) and (III13).

Among the cationic direct dyes of formula (III') which can be used in the dye compositions in accordance with the invention, mention may be made more particularly of the compounds corresponding to the structures (III'1) to (III'3) below:



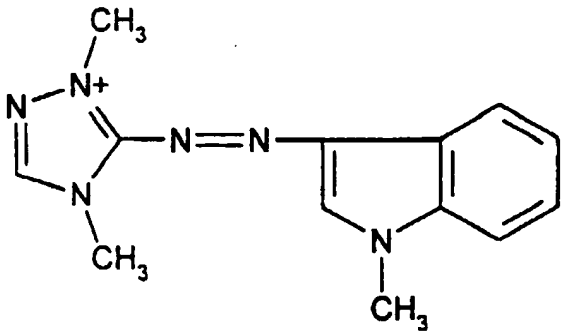
Cl⁻ (III'1)

;



Cl⁻ (III'2)

; and



Cl⁻ (III'3)

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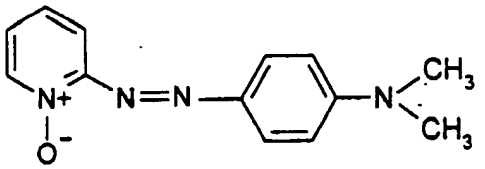
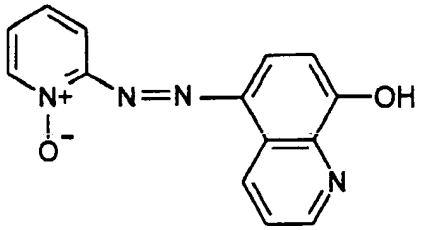
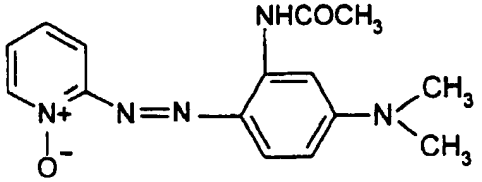
Among the cationic direct dyes of formula (IV) which can be used in the dye compositions in accordance with the invention, mention may be made more particularly of the compounds of structures $(IV)_1$ to $(IV)_{77}$ below:



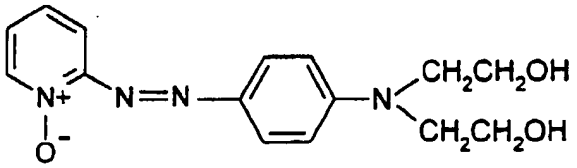
(IV)$_1$



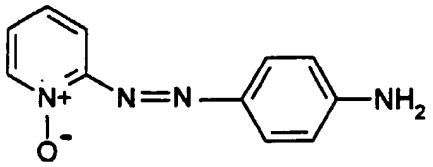
(IV)$_2$



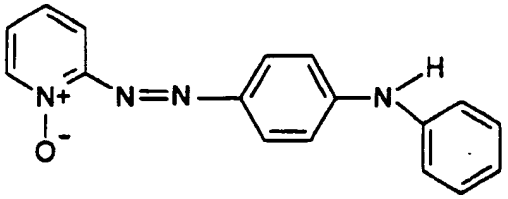
(IV)$_3$



(IV)$_4$



(IV)$_5$



(IV)$_6$

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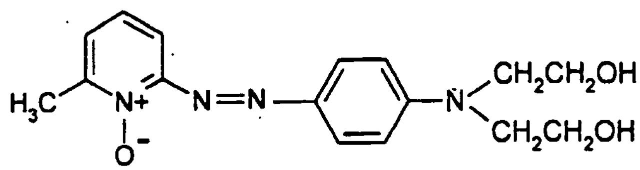
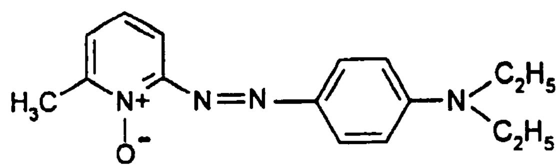
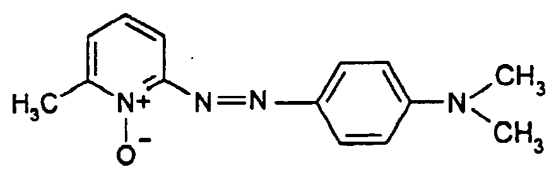


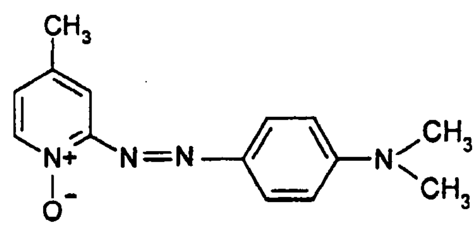
(IV)$_7$



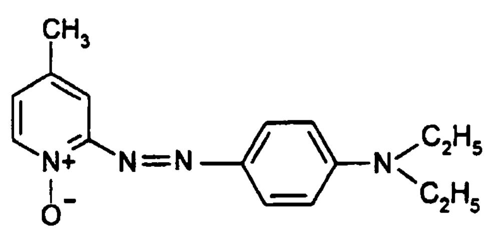
(IV)$_8$



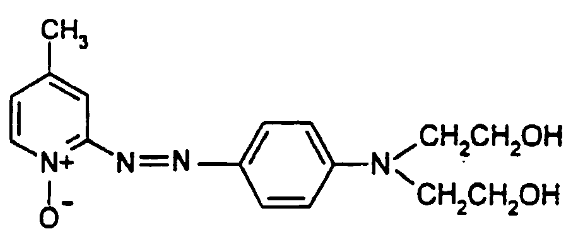
(IV)$_9$



(IV)$_{10}$



(IV)$_{11}$



(IV)$_{12}$

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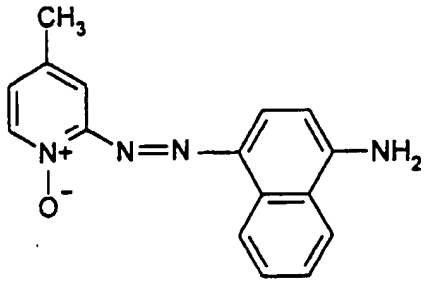
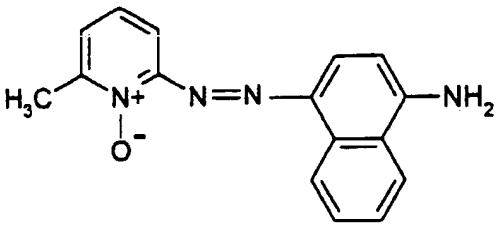
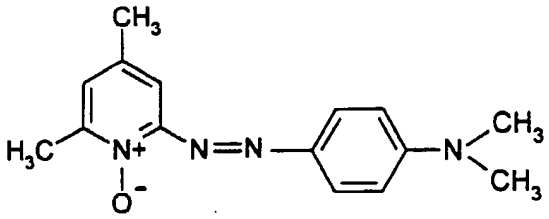


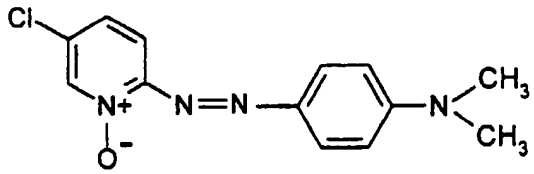
$(IV)_{13}$



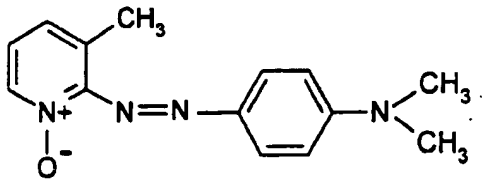
$(IV)_{14}$



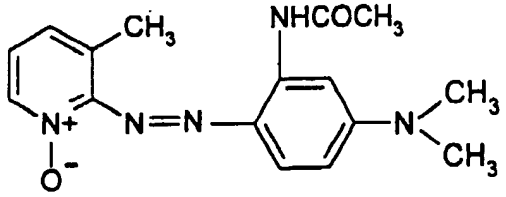
$(IV)_{15}$



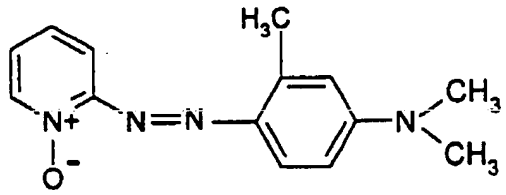
$(IV)_{16}$



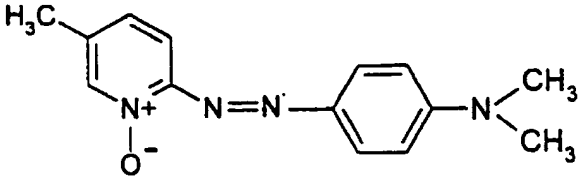
$(IV)_{17}$



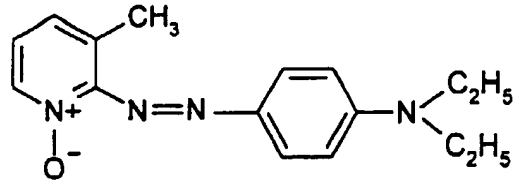
$(IV)_{18}$



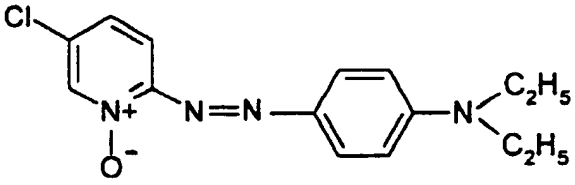
$(IV)_{19}$



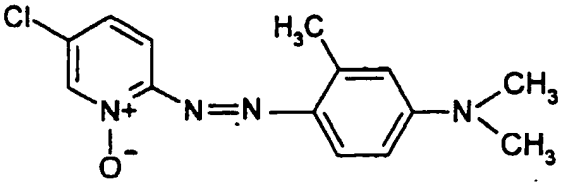
$(IV)_{20}$



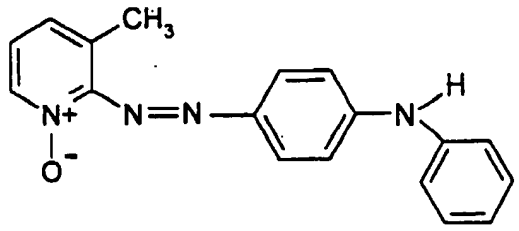
$(IV)_{21}$



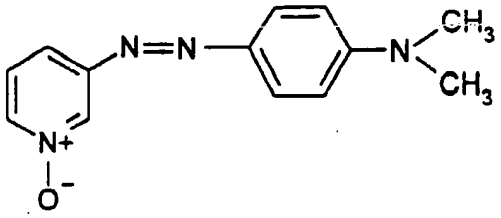
$(IV)_{22}$



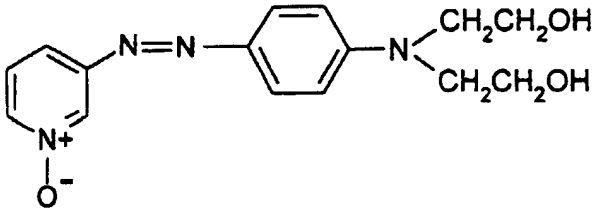
$(IV)_{23}$



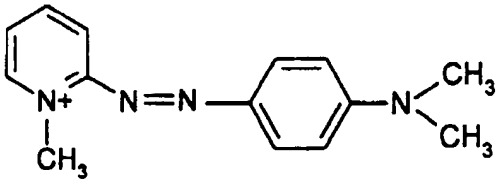
$(IV)_{24}$



$(IV)_{25}$

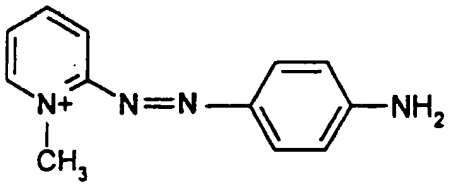


$(IV)_{26}$



$CH_3SO_4^-$

$(IV)_{27}$



$CH_3SO_4^-$

$(IV)_{28}$

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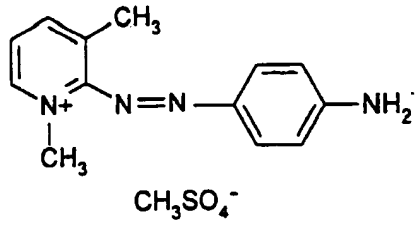
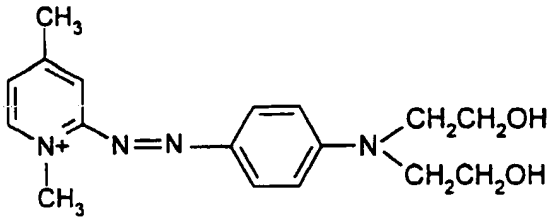
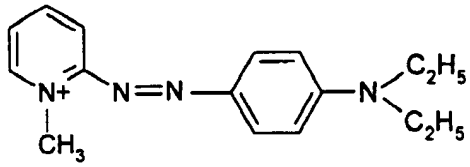


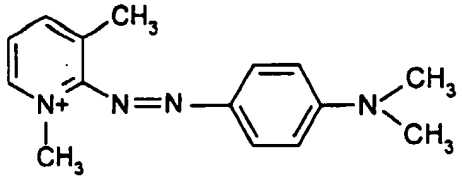
$CH_3SO_4^-$ $(IV)_{29}$



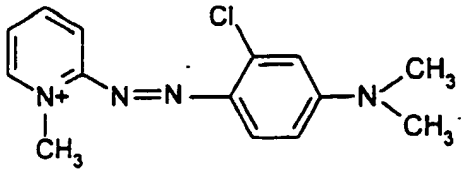
$CH_3SO_4^-$ $(IV)_{30}$



$CH_3SO_4^-$ $(IV)_{31}$



$CH_3SO_4^-$ $(IV)_{32}$



$CH_3SO_4^-$ $(IV)_{33}$

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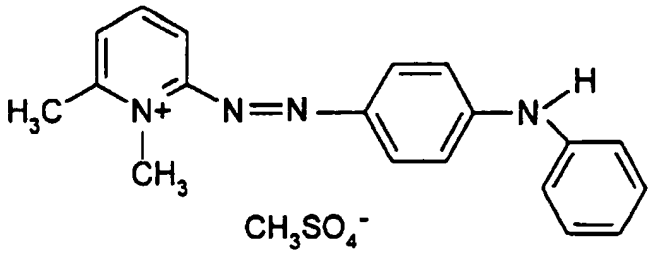
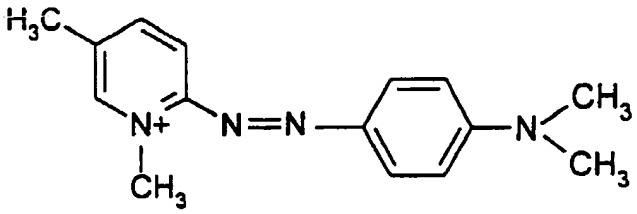


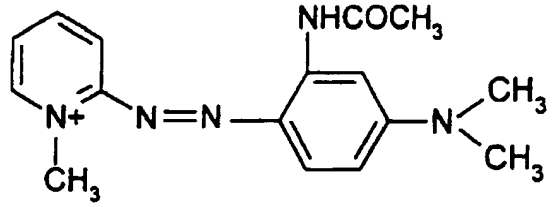
$CH_3SO_4^-$

$(IV)_{34}$



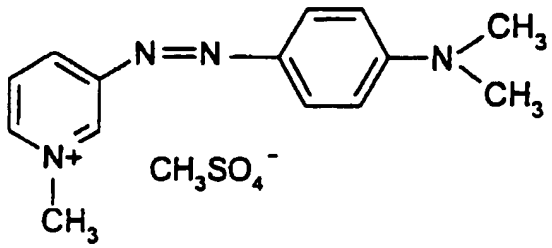
$CH_3SO_4^-$

$(IV)_{35}$



$CH_3SO_4^-$

$(IV)_{36}$



$CH_3SO_4^-$

$(IV)_{37}$

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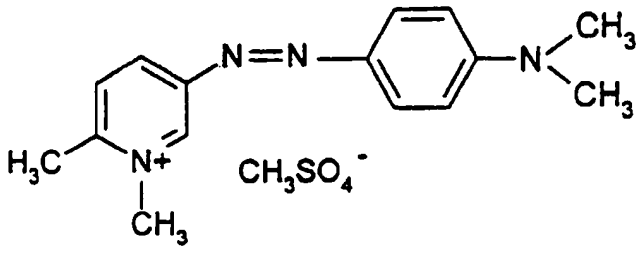
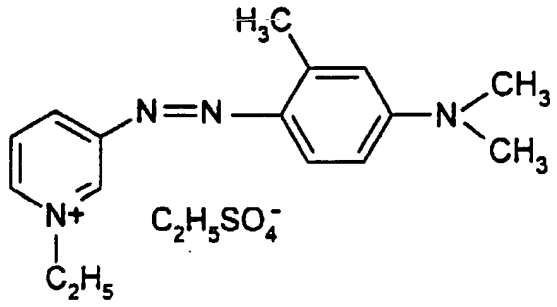
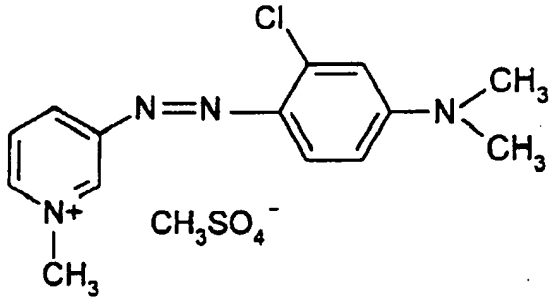


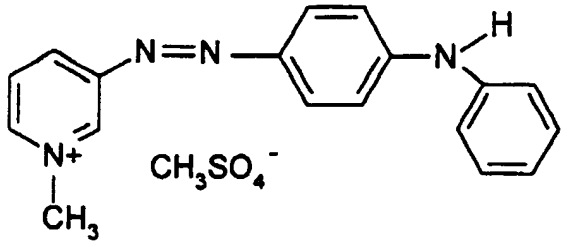
$(IV)_{38}$



$(IV)_{39}$



$(IV)_{40}$



$(IV)_{41}$

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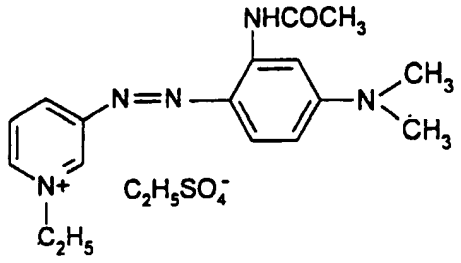
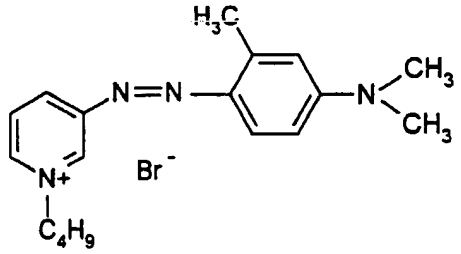
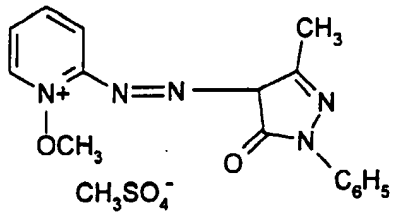


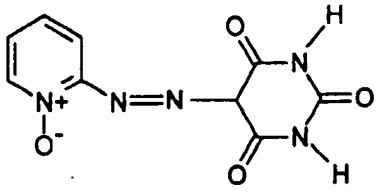
$(IV)_{42}$



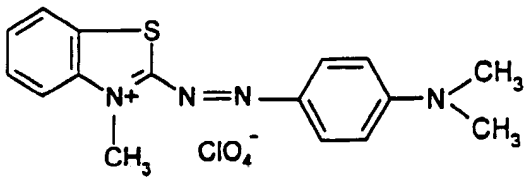
$(IV)_{43}$



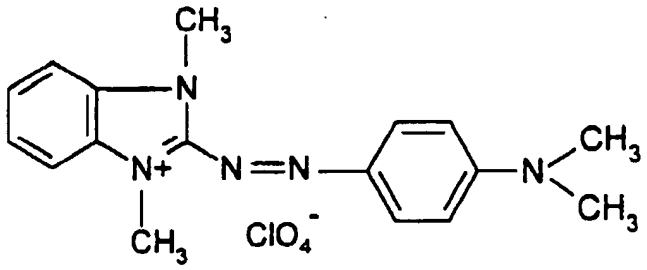
$(IV)_{44}$



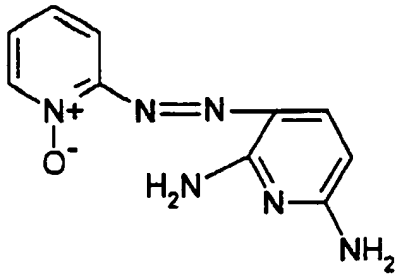
$(IV)_{45}$



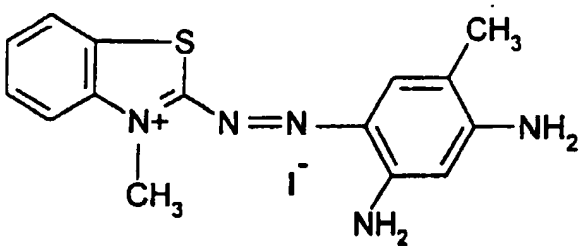
$(IV)_{46}$



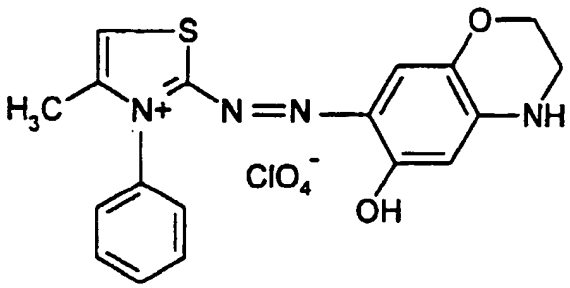
$(IV)_{47}$



$(IV)_{48}$



$(IV)_{49}$



$(IV)_{50}$

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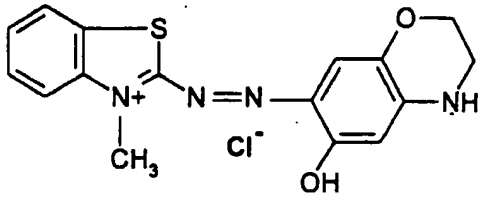
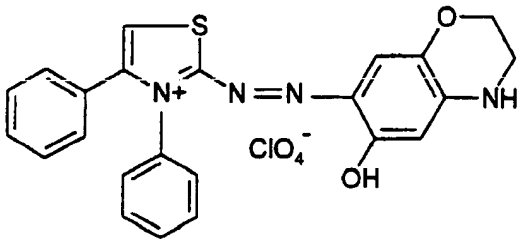
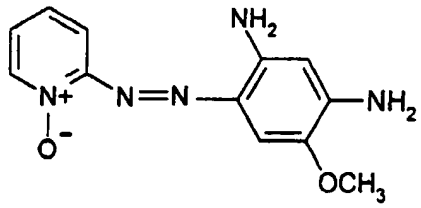


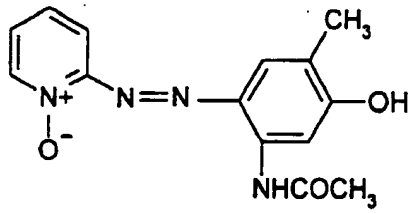
$(IV)_{51}$



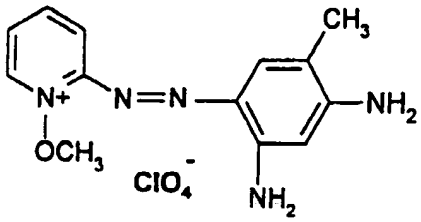
$(IV)_{52}$



$(IV)_{53}$



$(IV)_{54}$



$(IV)_{55}$

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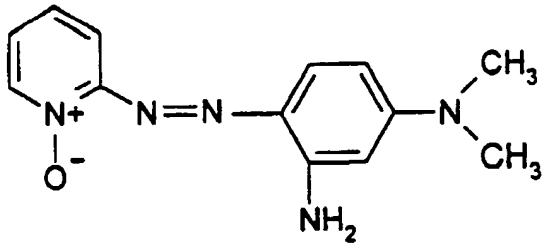
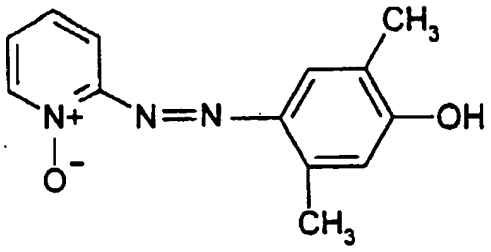
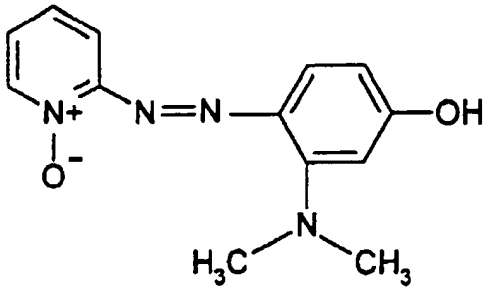


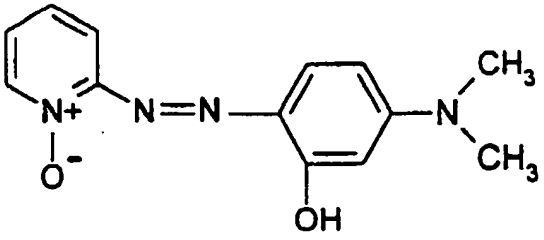
$(IV)_{56}$



$(IV)_{57}$



$(IV)_{58}$



$(IV)_{59}$

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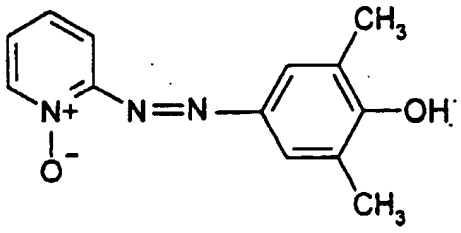
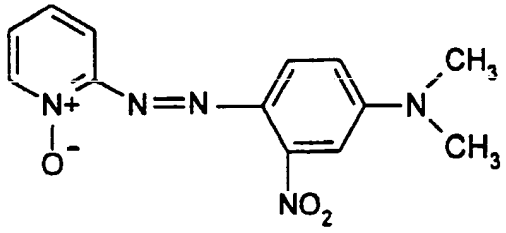
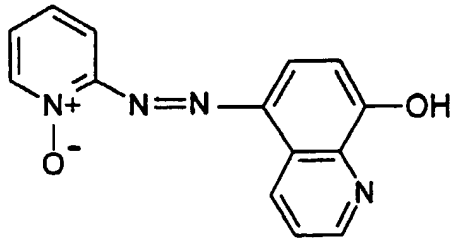


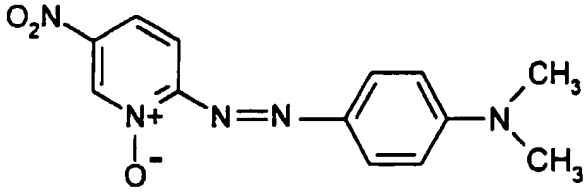
$(IV)_{60}$



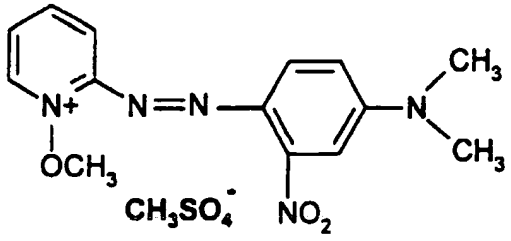
$(IV)_{61}$



$(IV)_{62}$



$(IV)_{63}$



$(IV)_{64}$

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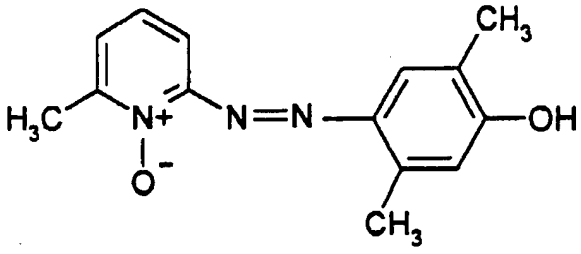
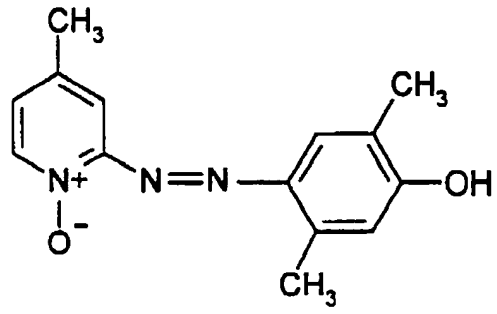
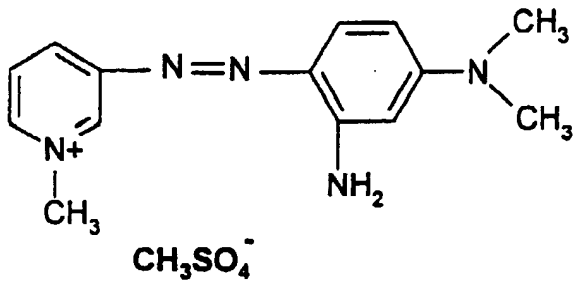


$(IV)_{65}$

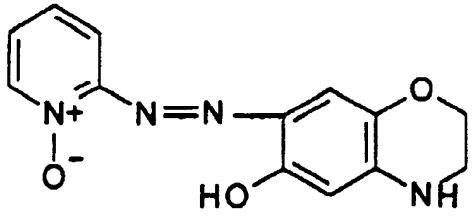


$(IV)_{66}$



$CH_3SO_4^-$

$(IV)_{67}$



$(IV)_{68}$

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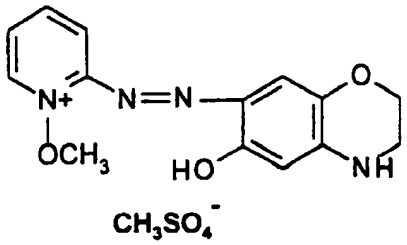
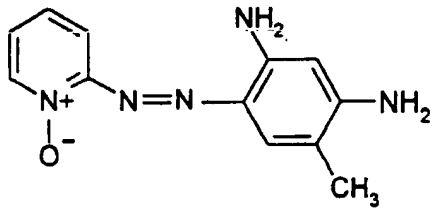
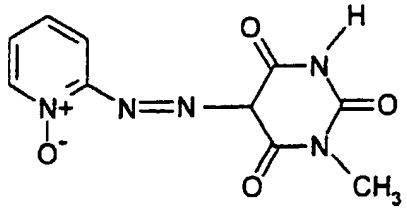


$CH_3SO_4^-$

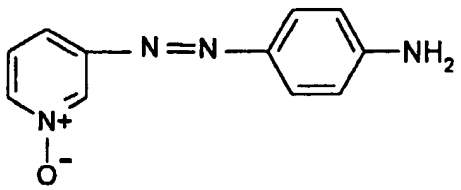
$(IV)_{69}$



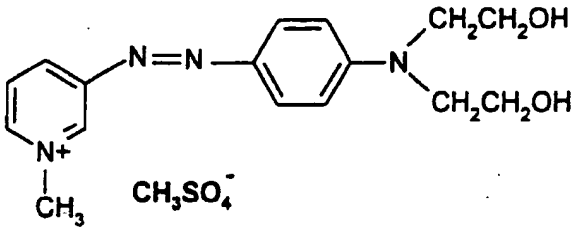
$(IV)_{70}$



$(IV)_{71}$



$(IV)_{72}$



$CH_3SO_4^-$

$(IV)_{73}$

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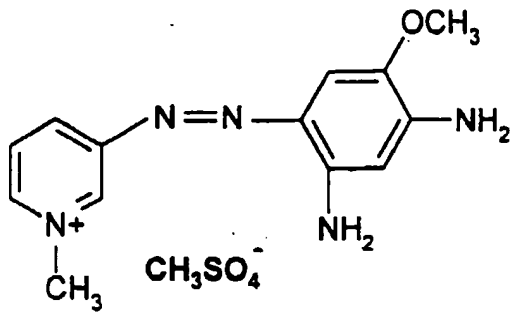
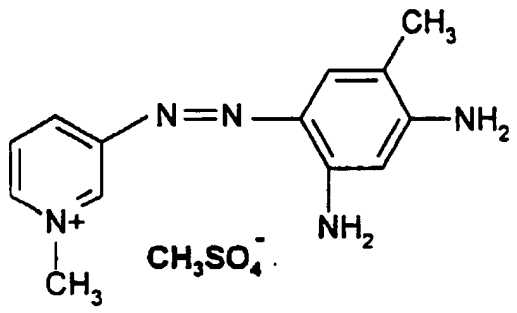
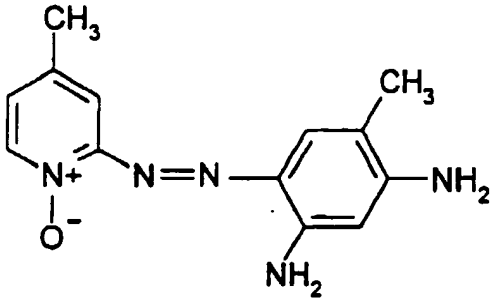


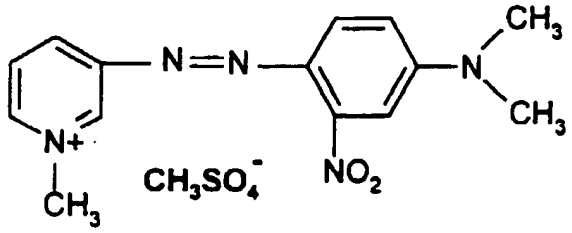
$(IV)_{74}$



$(IV)_{75}$



$(IV)_{76}$



$(IV)_{77}$

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The cationic direct dye(s) used according to the invention preferably represent(s) from 0.001 to 10% by weight approximately relative to the total weight of the dye composition and even more preferably from 0.005 to 5% by weight approximately relative to this weight.

(ii) The thickening polymer which can be used according to the present invention is chosen from the group consisting of:

$(ii)_1$ - nonionic amphiphilic polymers comprising at least one hydrophilic unit and at least one unit containing a fatty chain;

$(ii)_2$ - anionic amphiphilic polymers comprising at least one hydrophilic unit and at least one unit containing a fatty chain;

$(ii)_3$ - cationic amphiphilic polymers comprising at least one hydrophilic unit and at least one unit containing a fatty chain.

The nonionic amphiphilic polymers comprising at least one hydrophilic unit and at least one unit containing a fatty chain **$(ii)_1$**, used according to the invention, are preferably chosen from:

$(ii)_1$(a) celluloses modified with groups comprising at least one fatty chain; mention may be made, by way of example, of:

- hydroxyethylcelluloses modified with groups comprising at least one fatty chain, such as alkyl, arylalkyl or alkylaryl groups or mixtures thereof, and in which the alkyl groups are preferably C_8-C_{22}, such as the product Natrosol Plus

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Grade 330 CS (C_{16} alkyls) sold by the company Aqualon, or the product Bermocoll EHM 100 sold by the company Berol Nobel,

- hydroxyethylcelluloses modified with groups comprising at least one polyalkylene glycol alkylphenyl ether group, such as the product Amercell Polymer HM-1500 (polyethylene glycol (15) nonylphenyl ether) sold by the company Amerchol.

(ii)$_1$(b) hydroxypropylguars modified with groups comprising at least one fatty chain, such as the product Esaflor HM 22 (C_{22} alkyl chain) sold by the company Lamberti, and the products Miracare XC95-3 (C_{14} alkyl chain) and RE205-1 (C_{20} alkyl chain) sold by the company Rhône-Poulenc.

(ii)$_1$(c) polyurethane ethers comprising at least one fatty chain such as C_8-C_{30} alkyl or alkenyl groups, for instance the products Dapral T 210 and Dapral T 212 sold by the company Akzo.

(ii)$_1$(d) copolymers of vinylpyrrolidone and of hydrophobic monomers containing a fatty chain;

mention may be made, by way of example, of:

- the products Antaron V216 or Ganex V216 (vinylpyrrolidone/hexadecene copolymer) sold by the company I.S.P.

- the products Antaron V220 or Ganex V220 (vinylpyrrolidone/eicosene copolymer) sold by the company I.S.P.

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(ii)$_1$(e) copolymers of C_1-C_6 alkyl methacrylates or acrylates and of amphiphilic monomers comprising at least one fatty chain, such as, for example, the oxyethylenated methyl methacrylate/stearyl acrylate copolymer sold by the company Goldschmidt under the name Antil 208.

(ii)$_1$(f) copolymers of hydrophilic methacrylates or acrylates and of hydrophobic monomers comprising at least one fatty chain, such as, for example, the polyethylene glycol methacrylate/lauryl methacrylate copolymer.

The anionic amphiphilic polymers **(ii)$_2$** can be chosen from those:

(ii)$_2$(a) comprising at least one hydrophilic unit and at least one allyl ether unit containing a fatty chain, and preferably from those in which the hydrophilic unit comprising an unsaturated ethylenic anionic monomer, more particularly of a vinylcarboxylic acid and most particularly of an acrylic acid, a methacrylic acid or mixtures thereof, and in which the allyl ether unit containing a fatty chain corresponds to the monomer of formula (V) below:

$$CH_2=C\ R'CH_2\ O\ B_n\ R \qquad (V)$$

in which R' denotes H or CH_3, B denotes an ethylenoxy radical, n is zero or denotes an integer ranging from 1 to 100, R denotes a hydrocarbon-based radical chosen from alkyl and cycloalkyl radicals comprising from 8 to 30 carbon atoms, preferably

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10 to 24 and even more particularly from 12 to 18 carbon atoms, and most particularly a C_{10}-C_{24} alkyl radical.

One unit of formula (V) which is more particularly preferred according to the present invention is a unit in which R' denotes H, n is equal to 10 and R denotes a stearyl (C_{18}) radical.

Anionic amphiphilic polymers of this type are described and prepared according to an emulsion polymerization process in patent EP-0,216,479 B2.

Among the said anionic amphiphilic polymers cited **(ii)$_2$(a)** it is particularly preferred according to the invention to use the polymers formed from 20 to 60% by weight of acrylic acid and/or methacrylic acid, from 5 to 60% by weight of lower alkyl (meth)acrylates, from 2 to 50% by weight of allyl ether containing a fatty chain of formula (I), and from 0 to 1% by weight of a crosslinking agent which is a well known copolymerizable polyethylenic unsaturated monomer, such as diallyl phthalate, allyl (meth)acrylate, divinylbenzene, (poly)ethylene glycol dimethacrylate and methylenebisacrylamide.

Among the latter polymers, the ones most particularly preferred are the crosslinked terpolymers of methacrylic acid, of ethyl acrylate, of polyethylene glycol (10 EO) stearyl ether (Steareth-10), in particular those sold by the company Allied Colloids under the names Salcare SC 80 and Salcare SC 90 which are aqueous 30% emulsions of a crosslinked terpolymer of methacrylic acid, of ethyl acrylate and

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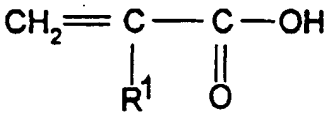
of Steareth-10 allyl ether (40/50/10).

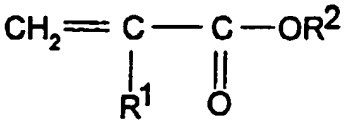
The anionic amphiphilic polymers **(ii)$_2$** can also be chosen from those:

(ii)$_2$(b) comprising at least one hydrophilic unit of unsaturated olefinic carboxylic acid type, and at least one unit containing a fatty chain exclusively of (C_{10}-C_{30})alkyl ester of unsaturated carboxylic acid type, and preferably from those in which the hydrophilic unit of unsaturated olefinic carboxylic acid type corresponds to the monomer of formula (VI) below:



(VI)

in which formula R^1 denotes H or CH_3 or C_2H_5, i.e. acrylic acid, methacrylic acid or ethacrylic acid units, and in which the unit containing a fatty chain of (C_{10}-C_{30})alkyl ester of unsaturated carboxylic acid type corresponds to the monomer of formula (VII) below:



(VII)

in which formula R^1 denotes H or CH_3 or C_2H_5 (i.e. acrylate, methacrylate or ethacrylate units) and preferably H (acrylate units) or CH_3 (methacrylate units), R^2 denoting a C_{10}-C_{30} alkyl and preferably C_{12}-C_{22} alkyl radical.

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(C_{10}-C_{30})alkyl esters of unsaturated carboxylic acids in accordance with the invention comprise, for example, lauryl acrylate, stearyl acrylate, decyl acrylate, isodecyl acrylate, dodecyl acrylate and the corresponding methacrylates, lauryl methacrylate, stearyl methacrylate, decyl methacrylate, isodecyl methacrylate and dodecyl methacrylate.

Anionic amphiphilic polymers of this type **(ii)$_2$(b)** are described and prepared, for example, according to US patents 3,915,921 and 4,509,949.

Anionic amphiphilic polymers **(ii)$_2$(b)** which can be used in the context of the present invention can more particularly denote polymers formed from a mixture of monomers comprising:

(i) essentially acrylic acid and an ester of formula (VII) described above in which R^1 denotes H or CH_3, R^2 denoting an alkyl radical containing from 12 to 22 carbon atoms, and a crosslinking agent, such as, for example, those comprising 95 to 60% by weight of acrylic acid (hydrophilic unit), 4 to 40% by weight of C_{10}-C_{30} alkyl acrylate (unit containing a fatty chain) and 0 to 6% by weight of crosslinking polymerizable monomer, or 98 to 96% by weight of acrylic acid (hydrophilic unit), 1 to 4% by weight of C_{10}-C_{30} alkyl acrylate (unit containing a fatty chain) and 0.1 to 0.6% by weight of crosslinking polymerizable monomer,

(ii) essentially acrylic acid and lauryl methacrylate, such as the polymer formed

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from 66% by weight of acrylic acid and 34% by weight of lauryl methacrylate.

The said crosslinking agent is a monomer containing a group $CH_2=C<$ with at least one other polymerizable group whose unsaturated bonds are not conjugated to each other. Mention may be made in particular of polyallyl ethers such as, in particular, polyallylsucrose and polyallylpentaerythritol.

Among the said polymers cited in class **(ii)$_2$(b)**, the ones most particularly preferred according to the present invention are the products sold by the company Goodrich under the trade names Pemulen TR1, Pemulen TR2, Carbopol 1382 and even more preferably Pemulen TR1 and the product sold by the company S.E.P.C. under the name Coatex SX.

The cationic amphiphilic polymers **(ii)$_3$** used according to the invention are preferably chosen from quaternized cellulose derivatives and polyacrylates containing amino side groups.

The quaternized cellulose derivatives are, in particular,

(ii)$_3$(a) quaternized celluloses modified with groups comprising at least one fatty chain, such as alkyl, arylalkyl or alkylaryl groups comprising at least 8 carbon atoms, or mixtures thereof,

(ii)$_3$(b) quaternized hydroxyethylcelluloses modified with groups comprising at least one fatty chain, such as alkyl, arylalkyl or alkylaryl groups comprising at least 8

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carbon atoms, or mixtures thereof.

The polyacrylates containing amino side groups **(ii)$_3$(c)**, which may or may not be quaternized, contain, for example, hydrophobic groups such as Steareth-20 [polyoxyethylenated (20) stearyl alcohol].

The alkyl radicals borne by the above quaternized celluloses or hydroxycelluloses preferably comprise from 8 to 30 carbon atoms.

The aryl radicals preferably denote phenyl, benzyl, naphthyl or anthryl groups.

As examples of quaternized alkylhydroxyethyl-celluloses containing C_8-C_{30} fatty chains, mention may be made of the products Quatrisoft LM200, Quatrisoft LM-X529-18-A, Quatrisoft LM-X529-18-B (C_{12} alkyl) and Quatrisoft LM-X529-8 (C_{18} alkyl) sold by the company Amerchol and the products Crodacel QM, Crodacel QL (C_{12} alkyl) and Crodacel QS (C_{18} alkyl) sold by the company Croda.

As examples of polyacrylates containing amino side chains, mention may be made of the polymers 8781-124B or 9492-103 from the company National Starch.

It is more particularly preferred, according to the present invention, to use the amphiphilic polymers of nonionic type **(ii)$_1$** and of anionic type **(ii)$_2$** described above and even more particularly the amphiphilic polymers of class **(ii)$_1$(a)** and **(ii)$_2$(c)** and of class **(ii)$_2$(a)** and **(ii)$_2$(b)**.

The amphiphilic thickening polymers of nonionic, anionic or cationic type used

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in the compositions of the present invention are preferably present in a proportion of from 0.01 to 10% by weight approximately, in particular in a proportion of from 0.1 to 5% by weight approximately, relative to the total weight of the dye composition applied to the keratin fibres.

The medium which is suitable for dyeing (or support) generally comprising water or of a mixture of water and at least one organic solvent to dissolve the compounds which would not be sufficiently water-soluble. As organic solvents, mention may be made, for example, of C_1-C_4 lower alkanols such as ethanol and isopropanol; aromatic alcohols such as benzyl alcohol, as well as similar products and mixtures thereof.

The solvents can be present in proportions preferably of between 1 and 40% by weight approximately relative to the total weight of the dye composition, and even more preferably between 5 and 30% by weight approximately.

The pH of the dye composition in accordance with the invention is generally approximately between 2 and 11 and preferably approximately between 5 and 10. It can be adjusted to the desired value using acidifying or basifying agents usually used for dyeing keratin fibres.

Among the acidifying agents, mention may be made, by way of example, of inorganic or organic acids such as hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids such as acetic acid, tartaric acid, citric acid and lactic acid,

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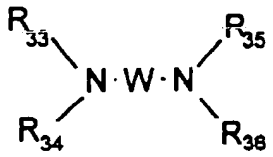
and sulphonic acids.

Among the basifying agents, mention may be made, by way of example, of aqueous ammonia, alkaline carbonates, alkanolamines such as mono-, di- and triethanolamine and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (VIII) below:



(VIII)

in which W is a propylene residue optionally substituted with a hydroxyl group or a C_1-C_6 alkyl radical; R_{33}, R_{34}, R_{35} and R_{36}, which may be identical or different, represent a hydrogen atom or a C_1-C_6 alkyl or C_1-C_6 hydroxyalkyl radical.

In addition to the cationic direct dye(s) (i) defined above, the dye composition in accordance with the invention can contain one or more additional direct dyes which can be chosen, for example, from nitrobenzene dyes, anthraquinone dyes, naphthoquinone dyes, triarylmethane dyes, xanthene dyes and azo dyes which are non-cationic.

When it is intended for oxidation dyeing, the dye composition in accordance with the invention contains, in addition to the cationic direct dye(s) (i), one or more oxidation bases chosen from the oxidation bases conventionally used for oxidation dyeing and among which mention may be made in particular of para-

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phenylenediamines, bis(phenyl)alkylenediamines, para-aminophenols, ortho-aminophenols and heterocyclic bases.

When they are used, the oxidation base(s) preferably represent(s) from 0.0005 to 12% by weight approximately relative to the total weight of the dye composition, and even more preferably from 0.005 to 6% by weight approximately relative to this weight.

When it is intended for oxidation dyeing, the dye composition in accordance with the invention can also contain, in addition to the cationic direct dye (i) and the thickening polymer (ii) as well as the oxidation bases, one or more couplers so as to modify the shades obtained or to enrich them with glints, by using the cationic direct dye(s) (i) and the oxidation base(s).

The couplers which can be used in the dye composition in accordance with the invention can be chosen from the couplers used conventionally in oxidation dyeing and among which mention may be made in particular of meta-phenylenediamines, meta-aminophenols, meta-diphenols and heterocyclic couplers.

When it is (they are) present, the coupler(s) preferably represent(s) from 0.0001 to 10% by weight approximately relative to the total weight of the dye composition, and even more preferably from 0.005 to 5% by weight approximately relative to this weight.

The dye composition in accordance with the invention can also contain

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various adjuvants conventionally used in compositions for dyeing the hair, such as antioxidants, penetrating agents, sequestering agents, fragrances, buffers, dispersing agents, surfactants, film-forming agents, ceramides, preserving agents, screening agents and opacifiers.

Needless to say, a person skilled in the art will take care to select this (these) optional complementary compound(s) such that the advantageous properties intrinsically associated with the dye composition in accordance with the invention are not, or are not substantially, adversely affected by the addition(s) envisaged.

The dye composition according to the invention can be in various forms, such as in the form of liquids, shampoos, creams or gels or any other form which is suitable for dyeing keratin fibres, and in particular human hair. It can be obtained by mixing, at the time of use, a composition, which may be pulverulent, containing the cationic direct dye(s) with a composition containing the specific thickening polymer.

When the combination of the cationic direct dye (i) and the thickening polymer (ii) according to the invention is used in a composition intended for oxidation dyeing (in which case one or more oxidation bases are used, optionally in the presence of one or more couplers) or when it is used in a composition intended for lightening direct dyeing, then the dye composition in accordance with the invention also comprises at least one oxidizing agent chosen, for example, from hydrogen peroxide, urea peroxide, alkali metal bromates, persalts such as perborates and

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persulphates, and enzymes such as peroxidases, lactases and two-electron oxidoreductases. It is particularly preferred to use hydrogen peroxide or enzymes.

Another subject of the invention is a process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, using the dye composition as defined above.

According to a first variant of this dyeing process in accordance with the invention, at least one dye composition as defined above is applied to the fibres, for a period which is sufficient to develop the desired coloration, after which the fibres are rinsed, optionally washed with shampoo, rinsed again and dried.

The time required to develop the coloration on the keratin fibres is generally between 3 and 60 minutes and even more specifically between 5 and 40 minutes.

According to a second variant of this dyeing process in accordance with the invention, at least one dye composition as defined above is applied to the fibres, for a period which is sufficient to develop the desired coloration, without final rinsing.

According to one specific embodiment of this dyeing process, and when the dye composition in accordance with the invention comprises at least one oxidation base and at least one oxidizing agent, the dyeing process comprises a first step which consists in separately storing, on the one hand, a composition (A1) comprising, in a medium which is suitable for dyeing, at least one cationic direct dye (i) as defined above and at least one oxidation base, and, on the other hand, a

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composition (B1) comprising, in a medium which is suitable for dyeing, at least one oxidizing agent, and then in mixing them together at the time of use, after which this mixture is applied to the keratin fibres, the composition (A1) or the composition (B1) containing the thickening polymer (ii) as defined above.

According to another specific embodiment of this dyeing process, and when the dye composition in accordance with the invention comprises at least one oxidizing agent, the dyeing process comprises a first step which consists in separately storing, on the one hand, a composition (A2) comprising, in a medium which is suitable for dyeing, at least one cationic direct dye (i) as defined above, and, on the other hand, a composition (B2) comprising, in a medium which is suitable for dyeing, at least one oxidizing agent, and then in mixing them together at the time of use, after which this mixture is applied to the keratin fibres, the composition (A2) or the composition (B2) containing the thickening polymer as defined above.

Another subject of the invention is a multi-compartment dyeing device or dyeing "kit" or any other multi-compartment packaging system, a first compartment of which comprises the composition (A1) or (A2) as defined above and a second compartment of which comprises the composition (B1) or (B2) as defined above. These devices can be equipped with means for dispensing the desired mixture onto the hair, such as the devices described in patent FR 2,586,913 in the name of the

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Applicant.

The examples which follow are intended to illustrate the invention without, however, limiting its scope.

EXAMPLES

EXAMPLES 1 to 3:

The three direct dyeing compositions given in the table below were prepared:

(all contents expressed in grams)

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	Example 1	Example 2	Example 3
Cationic direct dye of formula (I1)	0.2		
Cationic direct dye of formula (I14)		0.2	
Cationic direct dye of formula (IV27)			0.1
Diurethane (HMD) of oxyethylenated (66 EO) and oxypropylenated (14 PO) C_{16}-C_{18} alcohols, sold under the name Dapral T212 by the company Akzo	1.0 AM*		
Methacrylic acid/ethyl acrylate/Steareth 10 allyl ether crosslinked terpolymer sold as a 30% by weight emulsion under the name Salcare SC90 by the company Allied Colloid		1.0 AM*	
Acrylic acid/C_{10}-C_{30} alkyl acrylate crosslinked copolymer sold under the name Pemulen TR1 by the company Goodrich			1.0 AM*
Ethanol	10	10	10

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2-Amino-2-methyl-1-propanol qs	pH 9	pH 9	pH 9
Demineralized water qs	100	100	100

AM* denotes active material

The above compositions were each applied for 30 minutes to locks of natural grey hair containing 90% white hairs. The locks of hair were then rinsed, washed with a standard shampoo and then dried.

The locks were dyed in the following shades:

Examples	Shades obtained
1	Bright red
2	Bright orange
3	Bright purple

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